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METHOD AND APPARATUS FOR ALD DEPOSITION

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Respectfully submitted,

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METHOD AND APPARATUS FOR ALD DEPOSITION

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## METHOD AND APPARATUS FOR ALD DEPOSITION

### BACKGROUND OF THE DISCLOSURE

#### 5 Field of the Invention

The present invention relates to formation of one or more barrier layers and, more particularly, to one or more barrier layers formed using chemisorption techniques.

#### 10 Description of the Background Art

In manufacturing integrated circuits, one or more barrier layers are often used to inhibit diffusion of one or more materials in metal layers, as well as other impurities from intermediate dielectric layers, into elements underlying such barrier layers, such as transistor gates, capacitor dielectrics, transistor wells, 15 transistor channels, electrical barrier regions, interconnects, among other known elements of integrated circuits.

Though a barrier layer may limit to prevent migration of unwanted materials into such elements, its introduction creates an interface at least in part between itself and one or more metal layers. For sub half-micron (0.5  $\mu\text{m}$ ) semiconductor 20 devices, microscopic reaction at an interface between metal and barrier layers can cause degradation of integrated circuits, including but not limited to increased electrical resistance of such metal layers. Accordingly, though barrier layers have become a component for improving reliability of interconnect metallization schemes, it is desirable to mitigate "side effects" caused by introduction of such 25 barrier layers.

Compounds of refractory metals such as, for example, nitrides, borides, and carbides are targets as diffusion barriers because of their chemical inertness and low resistivities (e.g., sheet resistivities typically less than about 200  $\mu\Omega\text{-cm}$ ). In particular, borides such as, including but not limited to titanium diboride ( $\text{TiB}_2$ ), 30 have been used as a barrier material owing to their low sheet resistivities (e. g., resistivities less than about 150  $\mu\Omega\text{-cm}$ ).

Boride barrier layers are conventionally formed using chemical vapor deposition (CVD) techniques. For example, titanium tetrachloride ( $TiCl_4$ ) may be reacted with diborane ( $B_2H_6$ ) to form titanium diboride ( $TiB_2$ ) using CVD. However, when Cl-based chemistries are used to form boride barrier layers, 5 reliability problems can occur. In particular, boride layers formed using CVD chlorine-based chemistries typically have a relatively high chlorine (Cl) content, namely, chlorine content greater than about 3 %. A high chlorine content is undesirable because migrating chlorine from a boride barrier layer into adjacent interconnection layer may increase contact resistance of such interconnection 10 layer and potentially change one or more characteristics of integrated circuits made therewith.

Therefore, a need exists for barrier layers for integrated circuit fabrication with little to no side effects owing to their introduction. Particularly desirable would be a barrier layer useful for interconnect structures.

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### SUMMARY OF THE INVENTION

An aspect of the present invention is film deposition for integrated circuit fabrication. More particularly, at least one element from a first precursor and at least one element from a second precursor is chemisorbed on a surface. The at 20 least one element from the first precursor and the at least one element from the second precursor are chemisorbed to provide a tantalum-nitride film. This sequence may be repeated to increase tantalum-nitride layer thickness. This type of deposition process is sometimes called atomic layer deposition (ALD). Such a tantalum-nitride layer may be used as a barrier layer.

25 Another aspect is forming the tantalum-nitride layer using in part annealing of at least one tantalum-nitride sublayer. This annealing may be done with a plasma or chemical treatment.

Another aspect is using a plasma source gas as a nitrogen precursor. The plasma source gas may be used to provide a plasma, which may be sequentially 30 reacted or co-reacted with a tantalum containing precursor.

These and other aspects of the present invention will be more apparent from the following description.

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## BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

FIGS. 1 and 4 depict schematic illustrations of exemplary portions of process systems in accordance with one or more integrated circuit fabrication aspects of the present invention;

FIGs. 2a-2c depict cross-sectional views of a substrate structure at different stages of integrated circuit fabrication;

FIGs. 3a-3c depict cross-sectional views of a substrate at different stages of chemisorption to form a barrier layer; and

FIG. 5 depicts a cross-sectional view of a substrate structure at different stages of integrated circuit fabrication incorporating one or more tantalum-nitride barrier sublayers post plasma anneal.

## DETAILED DESCRIPTION

FIG. 1 depicts a schematic illustration of a wafer processing system 10 that can be used to form one or more tantalum-nitride barrier layers in accordance with aspects of the present invention described herein. System 10 comprises process chamber 100, gas panel 130, control unit 110, along with other hardware components such as power supply 106 and vacuum pump 102. For purposes of clarity, salient features of process chamber 100 are briefly described below.

### 25 Process Chamber

Process chamber 100 generally houses a support pedestal 150, which is used to support a substrate, such as a semiconductor wafer 190, within process chamber 100. Depending on process requirements, semiconductor wafer 190 can be heated to some desired temperature or within some desired temperature range prior to layer formation using heater 170.

In chamber 100, wafer support pedestal 150 is heated by an embedded heating element 170. For example, pedestal 150 may be resistively heated by

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applying an electric current from an AC power supply 106 to heating element 170. Wafer 190 is, in turn, heated by pedestal 150, and may be maintained within a desired process temperature range of, for example, about 20<sup>0</sup>C to about 500<sup>0</sup>C.

Temperature sensor 172, such as a thermocouple, may be embedded in wafer support pedestal 150 to monitor the temperature of support pedestal 150 in a conventional manner. For example, measured temperature may be used in a feedback loop to control electric current applied to heating element 170 from power supply 106, such that wafer temperature can be maintained or controlled at a desired temperature or within a desired temperature range suitable for a process application. Support pedestal 150 may optionally be heated using one or more radiant heating elements, such as lamps, to heat a wafer.

Vacuum pump 102 is used to evacuate process gases from process chamber 100 and to help maintain a desired pressure or desired pressure range inside chamber 100. Orifice 120 through a wall of chamber 100 is used to introduce process gases into process chamber 100. Sizing of orifice 120 conventionally depends on the size of process chamber 100.

Orifice 120 is coupled to gas panel 130 in part by valve 125. Gas panel 130 is configured to receive and then provide a resultant process gas from two or more gas sources 135, 136 to process chamber 100 through orifice 120 and valve 125. Gas sources 135, 136 may store precursors in a liquid phase at room temperature, which are later heated when in gas panel 130 to convert them to a vapor-gas phase for introduction into chamber 100. Gas panel 130 is further configured to receive and then provide a purge gas from purge gas source 138 to process chamber 100 through orifice 120 and valve 125. While only one valve and orifice is shown, the chamber may be configured to include more than one orifice and more than one valve. The valves may be high speed valves, such as EC valves, or the valves may be pneumatically actuated shut-off valves which are capable of operating at fairly high speeds. Depending on the particular application, processing sequences according to the present invention utilize valve actuation speeds ranging from several seconds to only a few milliseconds. Valves 125 are computer controlled by control unit 110 (described in more detail below).

G E N E R A T E D - I M P R I M E M T

Control unit 110, such as a programmed personal computer, work station computer, and the like, is configured to control flow of various process gases through gas panel 130 as well as valve 125 during different stages of a wafer process sequence. Illustratively, control unit 110 comprises central processing unit (CPU) 112, support circuitry 114, and memory 116 containing associated control software 113. In addition to control of process gases through gas panel 130, control unit 110 may be configured to be responsible for automated control of other activities used in wafer processing - such as wafer transport, temperature control, chamber evacuation, among other activities, some of which are described 5 elsewhere herein.

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Control unit 110 may be one of any form of general purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. CPU 112 may use any suitable memory 116, such as random access memory, read only memory, floppy disk drive, hard disk, 15 or any other form of digital storage, local or remote. Various support circuits may be coupled to CPU 112 for supporting system 10. Software routines 113 as required may be stored in memory 116 or executed by a second computer processor that is remotely located (not shown). Bi-directional communications between control unit 110 and various other components of wafer processing 20 system 10 are handled through numerous signal cables collectively referred to as signal buses 118, some of which are illustrated in FIG. 1.

#### Barrier Layer Formation

FIGs. 2a-2c illustrate one exemplary embodiment of a tantalum-nitride barrier layer application for integrated circuit fabrication of an interconnect structure in accordance with one or more aspects of the present invention. For purposes of clarity, substrate 200 refers to any workpiece upon which film processing is performed, and substrate structure 250 is used to denote substrate 200 as well as other material layers formed on substrate 200. Depending on the 25 processing stage, substrate 200 may be a silicon semiconductor wafer or other material layer, such as a dielectric material, including a low k dielectric material, which has been formed on wafer 190 (shown in FIG. 1).

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FIG. 2a is a cross-sectional view of a substrate structure 250, having a dielectric layer 202 formed thereon. Dielectric layer 202 may be an oxide, a silicon oxide, carbon doped silicon oxide, a fluoro-silicon, a porous dielectric, or other suitable dielectric formed and patterned to provide contact hole or via 202H extending to an exposed surface portion 202T of substrate 200. In the sectional view shown, the opening 202H is intended to represent both a via and a hole configuration. It will be understood by those with skill in the art that the present invention may also be used in a dual damascene process.

FIG. 2b shows a tantalum-nitride barrier layer 204 formed on substrate structure 250. The tantalum-nitride barrier layer 204 is formed by chemisorbing monolayers of a tantalum containing compound and a nitrogen containing compound on the substrate structure 250.

Referring to FIG. 2c, after the formation of tantalum-nitride barrier layer 204, a portion of layer 204 may be removed by etching in a well-known manner to expose a portion 202C of substrate 200. Portion 202C may be part of a transistor gate stack, a capacitor plate, a node, a conductor, or other conductive element. Next, contact layer 206 may be formed thereon, for example, to form an interconnect structure. Contact layer 206 may be selected from a group of aluminum (Al), copper (Cu), tungsten (W), and combinations thereof.

Contact layer 206 may be formed, for example, using chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, or a combination thereof. For example, an aluminum (Al) layer may be deposited from a reaction of a gas mixture containing dimethyl aluminum hydride (DMAH) and hydrogen (H<sub>2</sub>) or argon (Ar) or other DMAH containing mixtures, a CVD copper layer may be deposited from a gas mixture containing Cu<sup>+2</sup>(hfac)<sub>2</sub> (copper hexafluoro acetylacetone), Cu<sup>+2</sup>(fod)<sub>2</sub> (copper heptafluoro dimethyl octanediene), Cu<sup>+1</sup>hfac TMVS (copper hexafluoro acetylacetone trimethylvinylsilane), or combinations thereof, and a CVD tungsten layer may be deposited from a gas mixture containing tungsten hexafluoride (WF<sub>6</sub>) and a reducing gas. A PVD layer can be deposited from a copper target, an aluminum target, or a tungsten target.

Moreover, layer 206 may be a refractory metal compound including but not limited to titanium (Ti), tungsten (W), tantalum (Ta), zirconium (Zr), hafnium (Hf), molybdenum (Mo), niobium (Nb), vanadium (V), and chromium (Cr), among others. Conventionally, a refractory metal is combined with reactive species, such 5 as for example chlorine (Cl) or fluorine (F), and is provided with another gas to form a refractory metal compound. For example, titanium tetrachloride ( $TiCl_4$ ), tungsten hexafluoride ( $WF_6$ ), tantalum pentachloride ( $TaCl_5$ ), zirconium tetrachloride ( $ZrCl_4$ ), hafnium tetrachloride ( $HfCl_4$ ), molybdenum pentachloride ( $MoCl_5$ ), niobium pentachloride ( $NbCl_5$ ), vanadium pentachloride ( $VCl_5$ ), or 10 chromium tetrachloride ( $CrCl_4$ ) may be used as a refractory metal-containing compound gas.

Though layer 206 is shown as formed on layer 204, it should be understood that layer 204 may be used in combination with one or more other barrier layers formed by CVD or PVD. Accordingly, layer 204 need not be in 15 direct contact with layer 206, but an intervening layer may exist between layer 206 and layer 204. For example, in a copper interconnect application, a tantalum layer may be deposited over a tantalum nitride barrier layer. The tantalum layer may provide better adhesion between the tantalum nitride layer and the copper layer. As discussed in more detail below, a tantalum nitride layer deposited 20 according to the rapid chemical vapor deposition or ALD techniques disclosed herein, provide good barrier properties with low resistance at thickness around 10 angstroms. However, copper may adhere better to tantalum than to tantalum nitride.

Monolayers are chemisorbed by sequentially providing a tantalum 25 containing compound and a nitrogen containing compound to a process chamber. Monolayers of a tantalum containing compound and a nitrogen containing compound are alternately chemisorbed on a substrate 300 as illustratively shown in FIGs. 3a-3c.

FIG. 3a depicts a cross-sectional view of an exemplary portion of substrate 300 in a stage of integrated circuit fabrication, and more particularly at a stage of barrier layer formation. Tantalum layer 305 is formed by chemisorbing a tantalum-containing compound on surface portion 300T of substrate 300 by

introducing a pulse of a tantalum containing gas 135 into process chamber 100 (shown in FIG. 1). Tantalum containing gas 135 (shown in FIG. 1) may be a tantalum based organo-metallic precursor or a derivative thereof. Examples of such precursors include but are not limited to pentaethylmethylamino-tantalum 5 (PEMAT;  $Ta[N(C_2H_5CH_3)_2]_4$ ), pentadiethylamino-tantalum (PDEAT), pentadimethylamino-tantalum (PDMAT), and any and all of derivatives of PEMAT, PDEAT, or PDMAT. Other tantalum containing precursors include without limitation  $Ta(NMe_2)_5$ ,  $Ta(NEt_2)_5$ , TBTDET ( $Ta(NEt_2)_3$  or  $C_{16}H_{39}N_4Ta$ ), tantalum halides for example  $TaX_5$  where X is florine (F), bromine (Br) or chlorine (Cl), and 10 derivatives thereof.

Wafer 190 is maintained approximately below a thermal decomposition temperature of a selected tantalum precursor or a derivative thereof to be used and maintained at a pressure of less than about 100 Torr, preferably between about 1 and about 10 Torr. Wafer 190 may be heated by heating element 170. 15 An exemplary temperature range for precursors identified herein is about 20 to about 400 degrees Celsius ( $^0C$ ). For example, a temperature in a range of about 150 $^0C$  to about 300 $^0C$  may be used for PEMAT, while a temperature in a range of about 175 $^0C$  to about 250 $^0C$  may be used for PDMAT. Other precursors may have similar ranges, but it is believed that most tantalum precursors recited herein 20 can be deposited in a temperature range between about 20 $^0C$  and about 400 $^0C$ .

Though temperatures below a thermal decomposition temperature may be used, it should be understood that other temperatures, namely those above the thermal decomposition temperature of a particular precursor, may also be used depending upon the application. An exemplary temperature range above a 25 thermal decomposition temperature is approximately 400 to approximately 600 $^0C$ . More generally, the wafer surface temperature of a wafer being processed needs to be high enough to induce significant chemisorption of precursors instead of physisorption, but low enough to prevent significant decomposition of precursors. If the amount of decomposition during each precursor deposition is significantly 30 less than a layer, then the primary growth mode will be ALD. Accordingly, such a film will tend to have ALD properties. However, it is possible if a precursor significantly decomposes, but an intermediate reactant is obtained preventing

further precursor decomposition after a layer of intermediate reactant is deposited, that an ALD growth mode may still be obtained.

While not wishing to be bound by theory, it is believed that this tantalum-containing precursor combines tantalum atoms with one or more reactive species.

- 5 During tantalum layer 305 formation, these reactive species form byproducts that are transported from process chamber 100 by vacuum system 102 while leaving tantalum deposited on surface portion 300T. However, composition and structure of precursors on a surface during atomic-layer deposition (ALD) is not precisely known. A precursor may be in an intermediate state when on a surface of wafer
- 10 190. For example, each layer may contain more than simply elements of tantalum (Ta) or nitrogen (N); rather, the existence of more complex molecules having carbon (C), hydrogen (H), and/or oxygen (O) is probable. Additionally, a surface may saturate after exposure to a precursor forming a layer having more or less than a monolayer of either tantalum (Ta) or nitrogen (N). This composition or
- 15 structure will depend on available free energy on a surface of wafer 190, as well as atoms or molecules involved. Once all available sites are occupied by tantalum atoms, further chemisorption of tantalum is blocked, and thus the reaction is self-limiting.

After layer 305 of a tantalum containing compound is chemisorbed onto substrate 300, excess tantalum containing compound is removed from process chamber 10 by vacuum system 102 (shown in FIG. 1). A purge gas 138 (shown in FIG. 1) is preferably continuously supplied to process chamber 10 to facilitate removal of excess tantalum containing compound. Examples of suitable purge gases include but are not limited to helium (He), nitrogen (N<sub>2</sub>), argon (Ar), and hydrogen (H<sub>2</sub>), among others, and combinations thereof that may be used. Alternatively, the purge gas 138 may be pulsed to the chamber between the introduction of the tantalum precursor and the reducing gas. In either regime, the pumping system operates to continuously evacuate the gases from the chamber. Further still, a purge gas can be omitted and chamber pumping may be relied upon to evacuate the chamber of each of the precursor gases, e.g., the tantalum precursor and the reducing gas or reaction gas.

DETAILED DESCRIPTION

One particular embodiment may be appreciated with continuing reference to FIGS. 3a-c and renewed reference to FIG. 1, after process chamber 100 has been purged of the tantalum precursor, a pulse of ammonia gas ( $\text{NH}_3$ ) 136 is introduced into process chamber 100. Process chamber 100 and wafer 190 may 5 be maintained at approximately the same temperature and pressure range as used for formation of layer 305.

In FIG. 3b, a layer 307 of nitrogen is illustratively shown as chemisorbed on tantalum layer 305 at least in part in response to introduction of ammonia gas 136. While not wishing to be bound by theory, it is believed that nitrogen layer 10 307 is formed in a similar self-limiting manner as is tantalum layer 305. Each tantalum layer 305 and nitrogen layer 307, introduced in any combination or sequence, contact one another form a sublayer 309, whether or not either or both or neither is a monolayer, less than a monolayer or several monolayers. Nitrogen comprising gases may include, but are not limited to, ammonia and other N 15 containing precursors such as gases having the general formula  $\text{N}_x\text{H}_y$ , where x and y are integers. Such gases include  $\text{N}_2\text{H}_4$ . Other gases may include  $\text{NH}_2\text{N}(\text{CH}_3)_2$ , among others. Alternatively, a plasma source may be employed to provide activated nitrogen comprising gases. For example, nitrogen may be provided into a remote plasma unit coupled to the chamber so that activated 20 nitrogen may be utilized in the deposition sequence.

After an ammonia gas compound is chemisorbed onto tantalum layer 305 on substrate 300 to form nitrogen monolayer 307, excess ammonia gas compound is removed from process chamber 10 by vacuum system 102. A pulse of purge gas 138 may be supplied to process chamber 10 to facilitate this removal if pulse purge process is used instead of a continuous purge process. 25

Thereafter, as shown in FIG. 3c, tantalum and nitrogen layer deposition in an alternating sequence may be repeated with interspersed purges until a desired layer 204 thickness is achieved. Tantalum-nitride layer 204 may, for example, have a thickness in a range of approximately 0.0002 microns (2 Å) to about 0.05 30 microns (500 Å), though a thickness of approximately 0.001 microns (10 Å) to about 0.005 microns (50 Å) may be a sufficient barrier. Moreover, a tantalum-nitride layer 204 may be used as a thin film insulator or dielectric, or may be used

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as a protective layer for example to prevent corrosion owing to layer 204 being relatively inert or non-reactive. Advantageously, layer 204 may be used to coat any of a variety of geometries.

In FIGs. 3a-3c, tantalum-nitride layer 204 formation is depicted as starting 5 with chemisorption of a tantalum containing compound on substrate 300 followed by chemisorption of a nitrogen containing compound. Alternatively, chemisorption may begin with a layer of a nitrogen containing compound on substrate 300 followed by a layer of a tantalum containing compound.

Pulse time for each pulse of a tantalum containing compound, a nitrogen 10 containing compound, and a purge gas (where no continuous purge gas is delivered) is variable and depends on volume capacity of a deposition chamber 100 employed as well as vacuum system 102 coupled thereto. Similarly, the time between each pulse is also variable and depends on volume capacity of process chamber 100 as well as vacuum system 102 coupled thereto. However, in 15 general, wafer 190 surface must be saturated by the end of a pulse time, where pulse time is defined as the time a surface is exposed to a precursor. There is some variability here, for example (1) a lower chamber pressure of a precursor will require a longer pulse time; (2) a lower precursor gas flow rate will require a longer time for chamber pressure to rise and stabilize requiring a longer pulse 20 time; and (3) a large-volume chamber will take longer to fill, longer for chamber pressure to stabilize thus requiring a longer pulse time. In general, precursor gases should not mix at or near the wafer surface to prevent co-reaction (a co-reactive embodiment is disclosed elsewhere herein), and, thus, at least one gas purge (continuous or pulsed) and/or pump evacuation between precursor pulses 25 should be used to prevent mixing.

Generally, a pulse time of less than about 1 second for a tantalum containing compound and a pulse time of less than about 1 second for a nitrogen containing compound is typically sufficient to chemisorb alternating monolayers that comprise tantalum-nitride layer 204 on substrate 300. A pulse time of less 30 than about 1 second for purge gas 138 is typically sufficient to remove reaction byproducts as well as any residual materials remaining in process chamber 100 in a pulse purge regime. In a continuos purge regime, about a 1 second interval

between tantalum precursor and nitrogen precursor introduction can be used to insure that residual gas of one precursor is evacuated before a second gas is introduced. The overall cycle time for each monolayer may be less than about 2 seconds.

5 Sequential deposition as described advantageously provides good step coverage and conformality, due to using a chemisorption mechanism for forming tantalum-nitride layer 204. With complete or near complete saturation after each exposure of wafer 190 to a precursor, each of uniformity and step coverage is approximately 100 percent. Because atomic layer deposition is used, precision  
10 controlled thickness of tantalum-nitride layer 204 may be achieved down to a single layer of atoms. Furthermore, in ALD processes, since it is believed that only about one atomic layer may be absorbed on a topographic surface per "cycle," deposition area is largely independent of the amount of precursor gas remaining in a reaction chamber once a layer has been formed. By "cycle," it is  
15 meant a sequence of pulse gases, including precursor and purge gases, and optionally one or more pump evacuations. Also, by using ALD, gas-phase reactions between precursors is minimized to reduce generation of unwanted particles.

One exemplary process for depositing a tantalum nitride film includes the  
20 use of PDMAT as the tantalum precursor and ammonia as the nitrogen precursor. The chamber is preferably maintained at a pressure in the range of about 1 to 2 Torr. The wafer is preferably maintained at a temperature in the range of about 175<sup>0</sup>C to about 250<sup>0</sup>C. More preferably, the temperature range may be between about 200<sup>0</sup>C and about 250<sup>0</sup>C. One chamber that can be used to deposit the  
25 tantalum nitride barrier layer is described in the chamber hardware disclosure (Attorney Docket No.: APPM/6222/PJS) attached hereto and filed herewith. The PDMAT is pulsed for a period of about 0.5 seconds and then the chamber is purged for about 0.5 seconds. Next, the ammonia is pulsed for a period of about 0.5 seconds and then the chamber is purged for 0.5 seconds. As a result, a  
30 deposition cycle lasts about 2 seconds.

The ampoule containing the PDMAT is preferably maintained at or below 120°C to vaporize the PDMAT. The gaseous PDMAT is delivered to the chamber through a gas line having valve disposed along its length.

It is believed that one embodiment of the barrier layer according to the 5 present invention formed from the PDAMT and ammonia process described herein is particularly advantageous at a thickness of less than about 15 angstroms. It is believed that the TaN barrier layer formed from this process is effective for both copper and low k dielectric applications at a thickness of only 10 angstroms. The resulting tantalum nitride layer was found to be pinhole free and 10 exhibit a smooth morphology as shown on page 10 of the attached presentation. The surface roughness is similar for each of the films which are 10 angstroms, 30 angstroms and 100 angstroms which illustrates that roughness is independent of thickness. The smooth surface exhibited provides for enhanced copper adhesion.

The films deposited according to the PDMAT and ammonia processes 15 demonstrated exceptional film uniformity. The film thickness is linearly proportional to the number of deposition cycles which results in accurate thickness control as shown on page 7 of the attached presentation. Thickness uniformity was found to be 1.8 percent for a 10 angstrom film and 2.1 percent for a 100 angstrom film on a 200mm substrate as shown on page 8 of the attached 20 presentation. The deposited films exhibited exceptionally conformal coverage, approaching 100 percent in at least some results.

When the barrier film was used to form an interconnect device, a Self Ionizing Plasma Physical Vapor Deposition (SIP PVD) copper seed layer was deposited over the barrier film. The inventors have found that the SIP physical 25 vapor deposition (PVD) copper seed layer exhibited a preferred {111} orientation on the deposited barrier layer. A crystal orientation of {111} is typically preferred because this orientation provides large grain sizes and exhibits good electromigration resistance as a result of the larger grain sizes. The SIP PVD copper seed layer may be deposited using a commercially available chamber 30 such as a SIP PVD chamber available from Applied Materials, Inc., located in Santa Clara, California.

The inventors have also found that TaN films deposited using PDMAT and ammonia according to the present invention exhibited an amorphous structure. The tantalum nitride barrier layer exhibited low via resistance for a 10 angstrom film. In contrast, barrier films deposited using conventional techniques such as ionized metal plasma PVD have a higher via resistance. Page 14 illustrates good yield for the ALD TaN film compared to the IMP TaN film. In addition, a 10 angstrom ALD TaN film demonstrated >5x time to failure compared with a 50 angstrom PVD Ta film. The lower resistance insures that the overall structure has a low resistance in copper applications, for example, where the ALD tantalum nitride barrier layer is disposed between two copper features..

In films having a thickness greater than 20 angstroms may benefit from plasma treatment or other chemical treatment following deposition. Barrier layers formed using embodiments of the present employing a plasma treatment following tantalum nitride deposition demonstrated improved via resistance. Page 23 of the presentation attached hereto illustrates that plasma treatment can decrease resistance and improve yield. The plasma treatment can include an argon plasma, a nitrogen plasma or a nitrogen and hydrogen plasma. Plasma treatment can be performed in the same deposition chamber in which the ALD tantalum nitride deposition occurs or in a different chamber. If the plasma treatment occurs in the same chamber it can be an in situ plasma or can be plasma delivered from a remote plasma source, such as a remote inductively coupled source or a microwave source.

Alternatively, the barrier layer may be exposed to a chemical treatment which can include expose to aluminum compounds or silicon compounds. These compounds can include, but are not limited to, DMAH, TMA, silane, dimethylsilane, trimethylsilane and other organosilane compounds. Chemical treatment can be performed at about 10 Torr at 400°C. Page 24 of the presentation shows an improvement in dewetting following chemical treatment compared with no chemical treatment. A TaN barrier layer  $\leq$  15 angstroms also enabled good grain growth of copper across the barrier layer. Page 21 demonstrates that copper grains can extend growth across the ALD TaN barrier layer. Copper exhibits epitaxial growth on the tantalum nitride barrier layer.

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In applications where additional barrier layer thickness is preferred or required, such as in low k dielectric applications, a PVD tantalum layer can be deposited over the ALD tantalum nitride layer. PVD tantalum deposited on the ALD barrier layer exhibited an alpha phase structure. Alpha phase tantalum is 5 lower in resistance than beta phase tantalum. Page 12 of the presentation illustrates that the resistance of PVD tantalum deposited on the ALD tantalum nitride barrier layer is much lower than the resistance of PVD tantalum deposited on oxide. Resistivity measurements confirm the lower resistance on ALD tantalum nitride.

10

### Co-Reaction

Though it has been described to alternate tantalum and nitrogen containing precursors and purging in between as applied in a sequential manner, another embodiment is to supply tantalum and nitrogen containing precursors 15 simultaneously. Thus, pulses of gases 135 and 136, namely, tantalum and nitrogen containing compounds, are both applied to chamber 100 at the same time. An example is PEMAT and NH<sub>3</sub>, though other tantalum-organic and nitrogen precursors may be used. Step coverage and conformality is good at approximately 95 to 100 percent for each. Moreover, deposition rate is 20 approximately 0.001 to 0.1 microns per second. Because a co-reaction is used, purging between sequential pulses of alternating precursors is avoided, as is done in ALD.

Wafer surface temperature is maintained high enough to sustain reaction between two precursors. This temperature may be below chemisorption 25 temperature of one or both precursors. Accordingly, temperature should be high enough for sufficient diffusion of molecules or atoms.

Wafer surface temperature is maintained low enough to avoid significant decomposition of precursors. However, more decomposition of precursors may be acceptable for co-reaction than for sequentially reacting precursors in an ALD 30 process. In general, wafer 190 surface diffusion rate of molecules or atoms should be greater than precursors' reaction rate which should be greater precursors' decomposition rate.

TUMBLE DRYER

For all other details, the above-mentioned description for sequentially applied precursors applies to co-reaction processing.

**Plasma Anneal**

5 After forming one or more combinations of layers 305 and 307, substrate structure 250 may be plasma annealed. Referring to FIG. 4, there is illustratively shown a schematic diagram of an exemplary portion of a process system 10P in accordance with an aspect of the present invention. Process system 10P is similar to process system 10, except for additions of one or more RF power  
10 supplies 410 and 412, showerhead 400, gas source 405, and matching network(s) 411. Notably, a separate plasma process system may be used. However, by using a CVD/PVD process system 10P, less handling of substrate structure 250 is involved, as layer 204 may be formed and annealed in a same chamber 100.

Showerhead 400 and wafer support pedestal 150 provide in part spaced  
15 apart electrodes. An electric field may be generated between these electrodes to ignite a process gas introduced into chamber 100 to provide a plasma 415. In this embodiment, argon is introduced into chamber 100 from gas source 405 to provide an argon plasma. However, if argon is used as a purge gas, gas source 405 may be omitted for gas source 138.

20 Conventionally, pedestal 150 is coupled to a source of radio frequency (RF) power source 412 through a matching network 411, which in turn may be coupled to control unit 110. Alternatively, RF power source 410 may be coupled to showerhead 400 and matching network 411, which in turn may be coupled to control unit 110. Moreover, matching network 411 may comprise different circuits  
25 for RF power sources 410 and 412, and both RF power sources 410 and 412 may be coupled to showerhead 400 and pedestal 150, respectively.

With continuing reference to FIG. 4 and renewed reference to FIG. 3c, substrate structure 250 having one or more iterations or tantalum-nitride sublayers 309 is located in process chamber 401. Argon (Ar) gas from gas source 405 is introduced into chamber 401 to plasma anneal substrate structure 250. While not wishing to be bound by theory, it is believed that plasma annealing reduces nitrogen content of one or more sublayers 309 by sputtering off nitrogen, which in

turn reduces resistivity. In other words, plasma annealing is believed to make tantalum-nitride layer 204 more tantalum-rich as compared to a non-plasma annealed tantalum-nitride layer 204. For example, a 1:1 Ta:N film may be annealed to a 2:1 Ta:N film. Tantalum-nitride films having a sheet resistance of 5 approximately equal to or less than 1200 micro-ohms-cm for 0.004 micron (40 Angstrom) films may be achieved.

It will be appreciated that other non-chemically reactive gases with respect to layer 204 may be used for physically displacing nitrogen from layer 204, including but not limited to neon (Ne), xenon (Xe), helium (He), and hydrogen 10 (H<sub>2</sub>). Generally, for a plasma-gas that does not chemically react with a tantalum-nitride film, it is desirable to have a plasma-gas atom or molecule with an atomic-mass closer to N than to Ta in order to have preferential sputtering of the N. However, a chemically reactive process may be used where a gas is selected which preferentially reacts for removal of N while leaving Ta.

15 Referring to FIG. 5, there is illustratively shown a cross sectional view of layer 204 after plasma annealing in accordance with a portion of an exemplary embodiment of the present invention. Plasma annealing may be done after formation of each nitrogen layer 307, or may be done after formation of a plurality of layers 307. With respect to the latter, plasma annealing may take place after 20 approximately every 0.003 to 0.005 microns (30 to 50 Angstroms) of layer 204 or after formation of approximately every 7 to 10 sublayers 309. However, plasma annealing may be done after formation of a sublayer 309, which is approximately 0.0001 to 0.0004 microns (1 to 4 Angstroms).

Plasma annealing with argon may be done with a wafer temperature in a 25 range of approximately 20 to 450 degrees Celsius and a chamber pressure of approximately 0.1 to 50 Torr with a flow rate of argon in a range of approximately 10 to 2000 standard cubic centimeters per minute (scdm) with a plasma treatment time approximately equal to or greater than one second. Generally, a tantalum-nitride film should be annealed at a temperature, which does not melt, sublime, or 30 decompose such a tantalum-nitride film.

The specific process conditions disclosed in the above description are meant for illustrative purposes only. Other combinations of process parameters

such as precursor and inert gases, flow ranges, pressure ranges and temperature ranges may be used in forming a tantalum-nitride layer in accordance with one or more aspects of the present invention.

Although several preferred embodiments, which incorporate the teachings 5 of the present invention, have been shown and described in detail, those skilled in the art can readily devise many other varied embodiments that still incorporate these teachings. By way of example and not limitation, it will be apparent to those skilled in the art that the above-described formation is directed at atomic layer CVD (ALCVD); however, low temperature CVD may be used as described with 10 respect to co-reacting precursors. Accordingly, layers 305 and 307 need not be monolayers. Moreover, it will be appreciated that the above described embodiments of the present invention will be particularly useful in forming one or more barrier layers for interconnects on semiconductor devices having a wide range of applications.

**Claims:**

- 1 1. A method of film deposition for integrated circuit fabrication, comprising:  
2       chemisorbing at least one element from a first precursor on a wafer  
3 surface;  
4       chemisorbing at least one element from a second precursor on the wafer  
5 surface; and  
6       the at least one element from the first precursor and the at least one  
7 element from the second precursor chemisorbed to provide a tantalum-nitride film.
- 1 2. The method of claim 1, wherein the first precursor and the second  
2 precursor are delivered sequentially to form the tantalum-nitride film.
- 1 3. The method of claim 1, wherein the first precursor and the second  
2 precursor are co-reacted to form the tantalum-nitride film.
- 1 4. A method of film deposition for integrated circuit fabrication, comprising:  
2       chemisorbing a first layer on a substrate, the first layer selected from a first  
3 tantalum layer and a first nitride layer;  
4       chemisorbing a second layer on the first layer, the second layer different  
5 from the first layer, the second layer selected from a second nitride layer and a  
6 second tantalum layer;  
7       the first layer and the second layer in combination providing a tantalum-  
8 nitride layer; and  
9       plasma annealing the tantalum-nitride layer to remove nitrogen therefrom.
- 1 5. The method of claim 4, wherein the plasma annealing is performed with a  
2 plasma source material chemically non-reactive to the tantalum-nitride layer and  
3 having an atomic mass closer to nitrogen than tantalum.

1 6. The method of claim 4, wherein the plasma annealing is performed with  
2 plasma source material selected from argon (Ar), xenon (Xe), helium (He), neon  
3 (Ne), hydrogen (H), nitrogen (N), and combinations thereof.

1 7. The method of claim 4, further comprising sequentially repeating the  
2 chemisorbing of the first layer and the second layer along with interspersed  
3 plasma anneals to provide the tantalum-nitride layer.

1 8. The method of claim 4, further comprising sequentially repeating the  
2 chemisorbing of the first layer and the second layer to provide the tantalum-nitride  
3 layer.

1 9. A method of film deposition for integrated circuit fabrication, comprising:  
2 providing a process system, the process system having a chamber;  
3 locating a substrate in the process chamber;  
4 providing a first reactive gas to the chamber;  
5 chemisorbing a first layer on the substrate at least in partial response to the  
6 first reactive gas, the first layer selected from a first tantalum layer and a first  
7 nitride layer;  
8 conditioning the chamber with at least one of a purge gas or an evacuation;  
9 providing a second reactive gas to the chamber; and  
10 chemisorbing a second layer on the first layer at least in partial response to  
11 the second reactive gas, the second layer different from the first layer, the second  
12 layer selected from a second nitride layer and a second tantalum layer.

1 10. The method of claim 9, wherein the first reactive gas is a tantalum  
2 containing gas.

1 11. The method of claim 10, wherein the tantalum containing gas is a tantalum  
2 based organo-metallic precursor or a derivative thereof.

1 12. The method of claim 11, wherein the tantalum based organo-metallic  
2 precursor is selected from pentaethylmethylamino-tantalum (PEMAT),  
3 pentadiethylamino-tantalum (PDEAT), pentadimethylamino-tantalum (PDMAT),  
4 and derivatives thereof.

1 13. The method of claim 11, wherein the tantalum based organo-metallic  
2 precursor is selected from  $Ta(NMe_2)_5$ ,  $Ta(NEt_2)_5$ , TBTDET, and tantalum halides.

1 14. The method of claim 10, wherein the second reactive gas is a nitrogen  
2 containing gas.

1 15. The method of claim 11, wherein the nitrogen containing gas is selected  
2 from an ammonia ( $NH_3$ ) gas and a nitrogen plasma source gas.

1 16. A method of film deposition for integrated circuit fabrication, comprising:  
2 providing at least one process system, the at least one process system  
3 having a chamber;  
4 locating a substrate in the chamber;  
5 providing a tantalum containing gas to the chamber;  
6 chemisorbing a first layer on the substrate at least in partial response to the  
7 tantalum containing gas;  
8 purging the chamber with at least one purge gas;  
9 providing a nitrogen containing gas to the chamber; and  
10 chemisorbing a second layer on the first layer at least in partial response to  
11 the ammonia containing gas;  
12 purging the chamber with the at least one purge gas; and  
13 forming a plasma for annealing the second layer.

1 17. The method of claim 16, further comprising sequentially repeating the  
2 chemisorbing of the first layer, the purging of the chamber and the chemisorbing  
3 of the second layer to provide multiple tantalum-nitride sublayers.

1 18. The method of claim 16, wherein the substrate is maintained approximately  
2 below a thermal decomposition temperature of the tantalum containing gas for  
3 chemisorbing of the first layer.

1 19. The method of claim 18, wherein the substrate is maintained approximately  
2 above a thermal decomposition temperature of the tantalum containing gas for the  
3 chemisorbing of the first layer.

1 20. The method of claim 18, wherein the purge gas is selected from the group  
2 of helium (He), neon (Ne), argon (Ar), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), and  
3 combinations thereof.

1 21. The method of claim 20, further comprising providing a plasma source gas  
2 to the chamber for ignition to provide the plasma.

1 22. The method of claim 21, wherein the plasma source gas and the at least  
2 one purge gas is argon (Ar).

1 23. The method of claim 18, wherein the nitrogen containing gas is ammonia  
2 (NH<sub>3</sub>).

1 24. A method of forming a barrier layer structure and an interconnect structure  
2 for use in integrated circuit fabrication, comprising:

3 providing a substrate having an oxide layer thereon, wherein the dielectric  
4 layer has recesses formed to expose portions of a surface of the substrate;

5 forming at least one tantalum-nitride layer on at least portions of the  
6 dielectric layer and the substrate surface, the at least one tantalum-nitride layer  
7 formed using a sequential chemisorption of tantalum containing and nitrogen  
8 containing precursor gases;

9 etching through portions of the at least one tantalum-nitride layer disposed  
10 within the recesses; and

11 depositing at least one metal at least in part in the recesses;

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12 wherein the at least one tantalum-nitride layer mitigates to prevents  
13 migration of elements of the at least one metal to the dielectric layer.

1 25. The method of claim 24, wherein the metal is selected from aluminum (Al),  
2 copper (Cu), tungsten (W) or a combination thereof.

1 26. The method of claim 24, wherein the at least one metal is a refractory  
2 metal selected from titanium (Ti), tungsten (W), vanadium (V), niobium (Nb),  
3 tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and molybdenum  
4 (Mo).

1 27. The method of claim 24, wherein the sequential chemisorption process  
2 comprises forming alternating layers of tantalum and nitrogen.

1 28. The method of claim 27, wherein the alternating layers of tantalum and  
2 nitrogen are formed by sequentially pulsing a tantalum containing gas and a  
3 nitrogen containing gas with purging therebetween.

1 29. A software routine on a computer storage media, the software routine,  
2 when executed, capable of causing a general purpose computer to control a  
3 process system to perform a method of thin film deposition comprising:

4 forming a tantalum-nitride layer, the tantalum-nitride layer formed using a  
5 sequential chemisorption process, the chamber configured for the sequential  
6 chemisorption process to have a temperature of less than about 400 °C, the  
7 sequential chemisorption process comprising in part alternating pulses of a  
8 tantalum containing gas and a nitrogen containing gas.

1 30. The software routine of claim 29, further comprising:  
2 controlling the process system to perform purges between formation of a  
3 tantalum layer and a nitride layer.

1 31. The software routine of claim 30, further comprising:

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2       controlling the process system to provide a plasma after forming the  
3   tantalum layer and the nitride layer.

1   32. A method of film deposition for integrated circuit fabrication, comprising:  
2       co-reacting a tantalum containing precursor and a nitrogen containing  
3   precursor to chemisorb a first layer on a wafer surface to provide a tantalum-  
4   nitride layer; and  
5       plasma annealing the tantalum-nitride layer to remove nitrogen therefrom.

1   33. The method of claim 32, wherein the plasma annealing is performed with a  
2   plasma source material chemically non-reactive to the tantalum-nitride layer and  
3   having an atomic mass closer to nitrogen than tantalum.

1   34. The method of claim 33, wherein the plasma annealing is performed with  
2   plasma source material selected from argon (Ar), xenon (Xe), helium (He),  
3   hydrogen (H), nitrogen (N), neon (Ne), and combinations thereof.

1   35. A method of film deposition for integrated circuit fabrication, comprising:  
2       providing a chamber;  
3       providing a plasma source gas containing nitrogen to the chamber;  
4       igniting the plasma source gas to provide a plasma;  
5       providing a tantalum containing gas to the chamber; and  
6       co-reacting the tantalum containing gas and the plasma to chemisorb on  
7   a wafer surface a tantalum-nitride layer.

1   36. A method of film deposition for integrated circuit fabrication, comprising:  
2       providing a chamber;  
3       providing a plasma source gas containing nitrogen to the chamber;  
4       igniting the plasma source gas to provide a plasma;  
5       chemisorbing a nitrogen layer on a substrate;  
6       providing a precursor gas containing tantalum to the chamber; and  
7       chemisorbing a tantalum layer on the substrate;

8 wherein the nitrogen layer and the tantalum layer in combination provide a  
9 tantalum-nitride layer.

1 37. A method of film deposition for integrated circuit fabrication, comprising:  
2 providing a process system, the process system having a chamber;  
3 locating a substrate in the process chamber;  
4 providing a tantalum containing gas to the chamber;  
5 providing a nitrogen containing gas to the chamber; and  
6 chemisorbing tantalum and nitrogen from the tantalum containing gas and  
7 the nitrogen containing gas to provide a tantalum-nitride layer on the substrate.

1 38. The method of claim 37, further comprising plasma annealing the tantalum-  
2 nitride layer.

1 39. The method of claim 37, wherein the tantalum containing gas is a tantalum  
2 based organo-metallic precursor or a derivative thereof.

1 40. The method of claim 39, wherein the tantalum based organo-metallic  
2 precursor is selected from pentaethylmethylamino-tantalum (PEMAT),  
3 pentadiethylamino-tantalum (PDEAT), pentadimethylamino-tantalum (PDMAT),  
4 and derivatives thereof.

1 41. The method of claim 39 wherein the tantalum based organo-metallic  
2 precursor is selected from  $Ta(NMe_2)_5$ ,  $Ta(NEt_2)_5$ , TBTDET, and tantalum halides.

1 42. The method of claim 39 wherein the nitrogen containing gas is ammonia  
2 ( $NH_3$ ).

1 43. The method of claim 37, wherein the substrate is maintained approximately  
2 below a thermal decomposition temperature of the tantalum containing gas.

TECHNICAL DRAWINGS

1 44. The method of claim 37, wherein the substrate is maintained approximately  
2 above a thermal decomposition temperature of the tantalum containing gas.

1 45. A method of forming a barrier layer structure and an interconnect structure  
2 for use in integrated circuit fabrication, comprising:

3 providing a substrate having an oxide layer thereon, wherein the dielectric  
4 layer has recesses formed to expose portions of a surface of the substrate;

5 forming at least one tantalum-nitride layer on at least portions of the  
6 dielectric layer and the substrate surface, the at least one tantalum-nitride layer  
7 formed using co-reaction chemisorption of tantalum containing and nitrogen  
8 containing precursor gases;

9 etching through portions of the at least one tantalum-nitride layer disposed  
10 within the recesses; and

11 depositing at least one metal at least in part in the recesses;

12 wherein the at least one tantalum-nitride layer mitigates to prevents  
13 migration of elements of the at least one metal to the dielectric layer.

1 46. The method of claim 45, wherein the at least one metal is selected from  
2 aluminum (Al), copper (Cu), tungsten (W) or a combination thereof.

1 47. The method of claim 45, wherein the at least one metal is a refractory  
2 metal selected from titanium (Ti), tungsten (W), vanadium (V), niobium (Nb),  
3 tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and molybdenum  
4 (Mo).

1 48. A software routine on a computer storage media, the software routine,  
2 when executed, capable of causing a general purpose computer to control a  
3 process system to perform a method of thin film deposition comprising:

4 forming a tantalum-nitride layer, the tantalum-nitride layer formed using co-  
5 reaction chemisorption of tantalum containing and nitrogen containing precursor  
6 gases at a temperature of less than about 300 °C.

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- 1 49. The software routine of claim 48, further comprising:
  - 2 providing an annealing plasma after forming the tantalum-nitride layer.
  
- 1 50. The software routine of claim 48, wherein the nitrogen containing precursor  
2 is a nitrogen plasma gas source.

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ABSTRACT OF THE INVENTION

A method of forming a tantalum-nitride layer (204) for integrated circuit fabrication is disclosed. Alternating or co-reacting pulses of a tantalum containing precursor and a nitrogen containing precursor are provided to a chamber (100) to form layers (305, 307) of tantalum and nitrogen. The nitrogen precursor may be a plasma gas source. The resultant tantalum-nitride layer (204) may be used, for example, as a barrier layer. As barrier layers may be used with metal interconnect structures (206), at least one plasma anneal on the tantalum-nitride layer may be performed to reduce its resistivity and to improve film property.

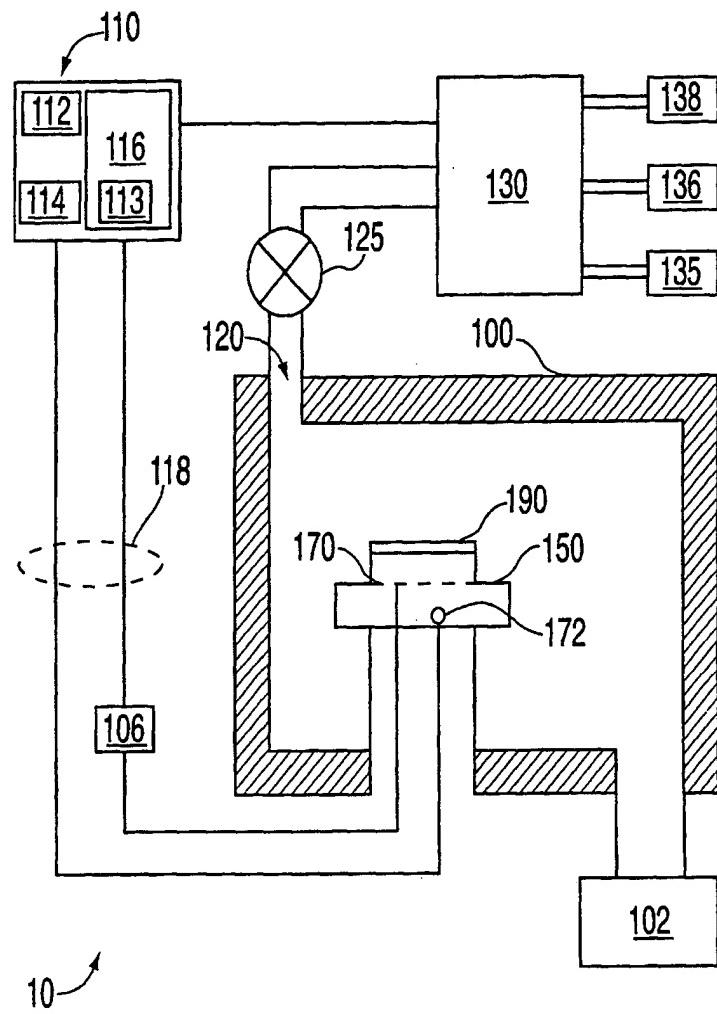


FIG. 1

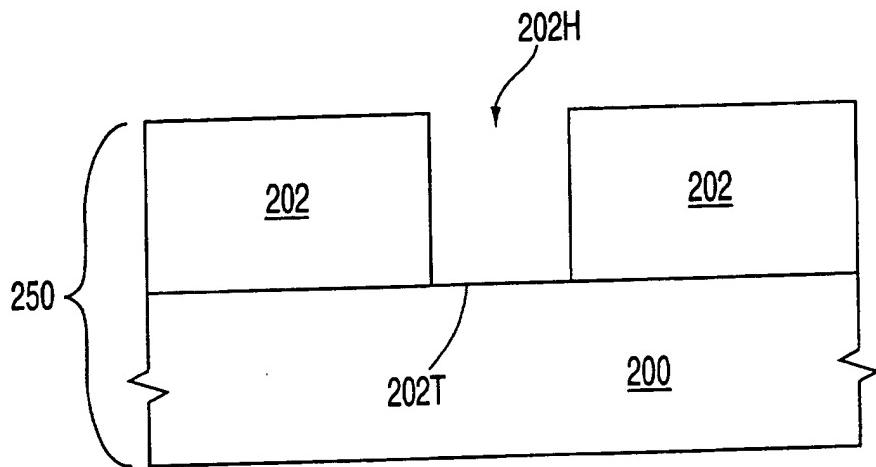


FIG. 2a

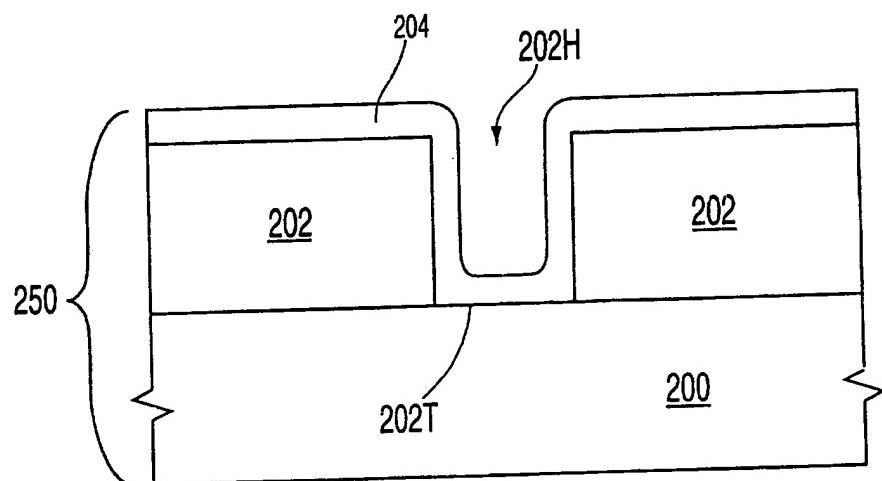


FIG. 2b

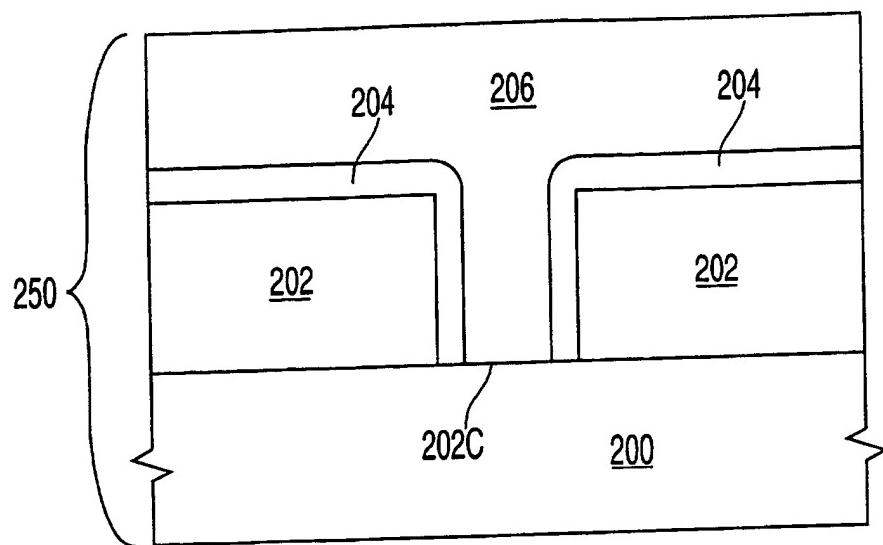


FIG. 2c

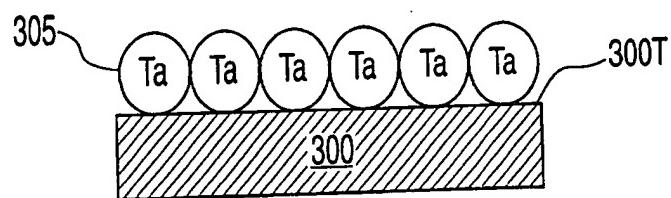


FIG. 3a

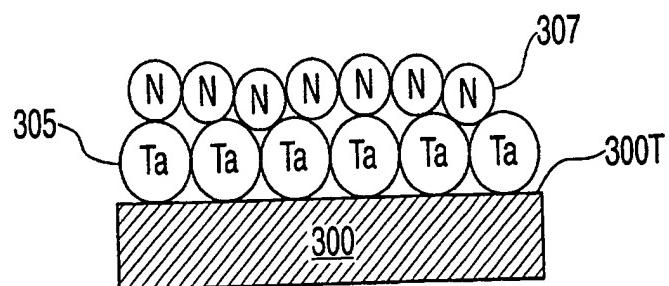


FIG. 3b

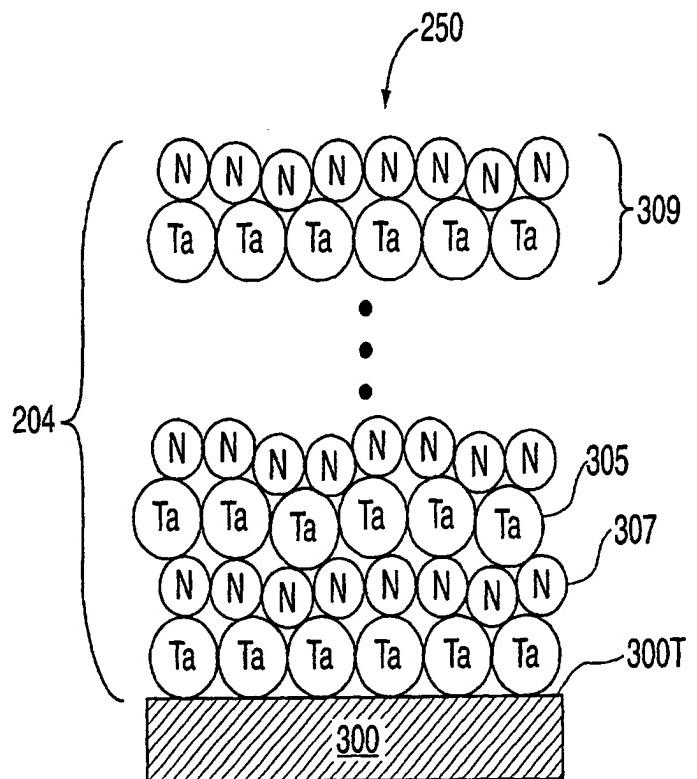


FIG. 3c

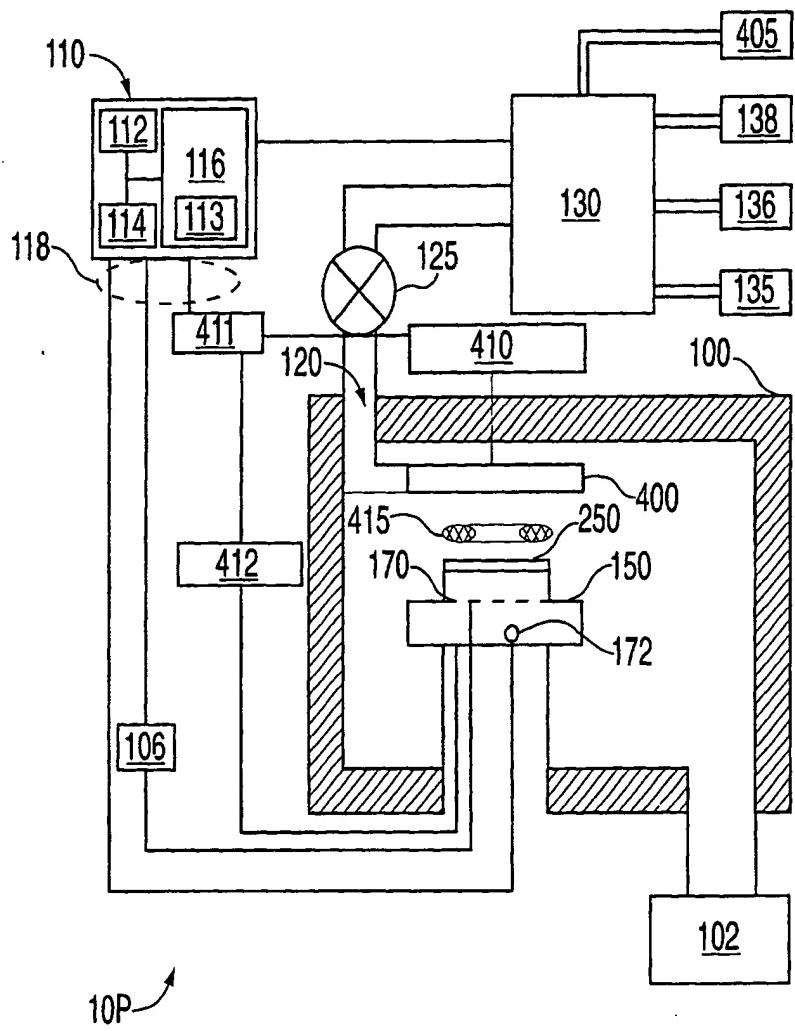


FIG. 4

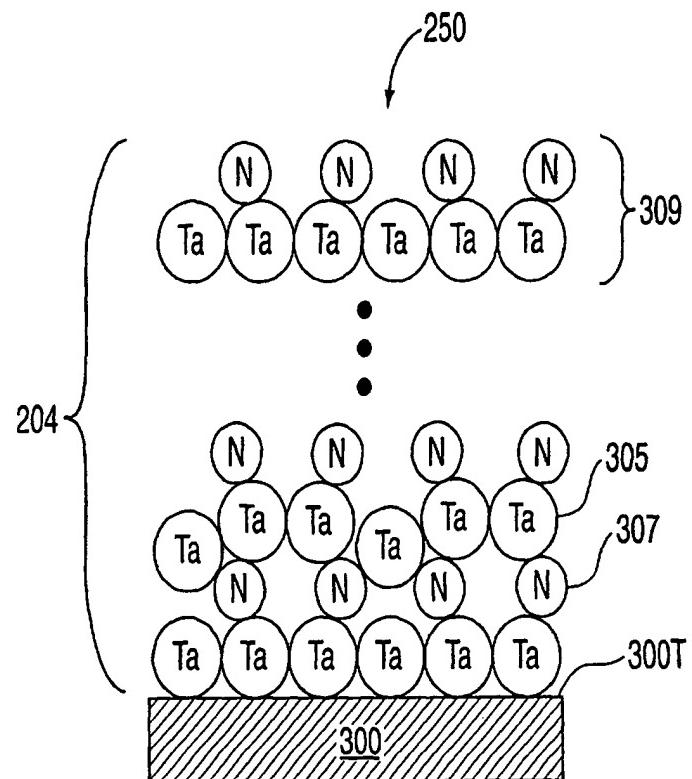


FIG. 5

# METHOD AND APPARATUS FOR ALD DEPOSITION

## BACKGROUND OF THE INVENTION

### **Field of the Invention**

[0001] Embodiments of the present invention generally relate to an apparatus and method for atomic layer deposition. More particularly, embodiments of the present invention relate to an improved gas delivery apparatus and method for atomic layer deposition.

### **Description of the Related Art**

[0002] Reliably producing sub-micron and smaller features is one of the key technologies for the next generation of very large scale integration (VLSI) and ultra large scale integration (ULSI) of semiconductor devices. However, as the fringes of circuit technology are pressed, the shrinking dimensions of interconnects in VLSI and ULSI technology have placed additional demands on the processing capabilities. The multilevel interconnects that lie at the heart of this technology require precise processing of high aspect ratio features, such as vias and other interconnects. Reliable formation of these interconnects is very important to VLSI and ULSI success and to the continued effort to increase circuit density and quality of individual substrates.

[0003] As circuit densities increase, the widths of vias, contacts, and other features, as well as the dielectric materials between them, decrease to sub-micron dimensions (e.g., less than 0.20 micrometers or less), whereas the thickness of the dielectric layers remains substantially constant, with the result that the aspect ratios for the features, i.e., their height divided by width, increase. Many traditional deposition processes have difficulty filling sub-micron structures where the aspect ratio exceeds 4:1, and particularly where the aspect ratio exceeds 10:1. Therefore, there is a great amount of ongoing effort being directed at the formation of substantially void-free and seam-free sub-micron features having high aspect ratios.

[0004] Atomic layer deposition is one deposition technique being explored for the deposition of material layers over features having high aspect ratios. One example of

atomic layer deposition comprises the sequential introduction of pulses of gases. For instance, one cycle for the sequential introduction of pulses of gases may comprise a pulse of a first reactant gas, followed by a pulse of a purge gas and/or a pump evacuation, followed by a pulse of a second reactant gas, and followed by a pulse of a purge gas and/or a pump evacuation. The term "gas" as used herein is defined to include a single gas or a plurality gases. Sequential introduction of separate pulses of the first reactant and the second reactant results in the alternating self-limiting chemisorption of monolayers of the reactants on the surface of the substrate and, thus, forms a monolayer of material for each cycle. The cycle may be repeated to a desired thickness of the deposited material. A pulse of a purge gas and/or a pump evacuation between the pulses of the first reactant gas and the pulses of the second reactant gas serves to reduce the likelihood of gas phase reactions of the reactants due to excess amounts of the reactants remaining in the chamber.

[0005] Figure 1 is a schematic cross-sectional view of a prior art chamber 100 adapted for chemical vapor deposition. The chamber 100 includes a substrate support 132 for supporting a substrate 136. A showerhead 140 is disposed over the substrate support 132 to provide a gas to the substrate 136. The showerhead 140 has a central gas inlet 144 for the injection of gases from a gas source (not shown) and has a plurality of holes 142 to accommodate the flow of the gas therethrough.

[0006] One problem with the use of chamber 100 for atomic layer deposition is that the showerhead 140 must delivery a gas to a large volume inside the chamber 100. For example, chamber 100 may be adapted to process 200 mm diameter substrates and may contain a volume of about 7,000 cm<sup>3</sup>. Therefore, the time period for a pulse of a reactant provided by the showerhead 140 is relatively long in order to provide a large enough amount of reactant to fill the chamber 100 and to absorb onto the substrate 136. In addition, the time period for a pulse of a purge gas and/or a pump evacuation is also relatively long in order to provide a large enough amount of the purge gas or to provide a long enough time period for the pump evacuation to remove excess reactants remaining in the chamber 100. Therefore, the throughput of atomic layer deposition of substrates through chamber 100 is slow.

[0007] Another problem with the use of chamber 100 for atomic layer deposition is that the flow of a gas from the showerhead 140 proceeds in a turbulent flow resulting in a non-uniform flow of the gas through the chamber 100. As a consequence, the time

period for a pulse of a gas, such as a reactant gas to absorb onto the substrate 136 or a purge gas to remove excess reactants and by-products, is relatively long in order to ensure that the gas reaches all areas of the chamber.

[0008] Therefore, there is a need for an improved apparatus and method of atomic layer deposition.

### SUMMARY OF THE INVENTION

[0009] Embodiments of the present invention relate to an improved gas delivery apparatus adapted for atomic layer deposition. One embodiment of the gas delivery apparatus comprises a covering having a passageway adapted for introduction of a gas flow and having a bottom surface sized and shaped to substantially cover a substrate disposed on a substrate support. The covering is adapted to be positioned adjacent a substrate defining a reaction zone between the bottom surface of the covering and the substrate. In one embodiment, the passageway comprises a conical section having at least one gas inlet adapted to receive a gas flow. In another embodiment, a channel is coupled to each gas inlet of the conical section and is adapted to provide a gas flow. The channel may be positioned to direct fluids horizontally, angled upwardly, or angled downwardly. In another embodiment, the channel may be further pointed at an angle from the center of the conical section.

[0010] One embodiment of a method of depositing a material layer over a substrate structure comprises providing at least one cycle of gases. One embodiment of a cycle of gases comprises providing a continuous flow of a purge gas and providing alternating pulses of at least two reactants. The continuous flow of a purge gas acts as a carrier gas during the pulses of the reactants. Another embodiment of a cycle of gases comprises providing a first continuous flow of a purge gas and pulses of a first reactant through a first channel and providing a second continuous flow of a purge gas and pulses of a second reactant through a second channel in which the pulses of the first reactant and pulses of the second reactant are alternating. The first and second continuous flows of the purge gas act as a carrier gas during the pulses of the first and the second reactants.

[0011] One embodiment of a method of delivering gases to a substrate in a substrate

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processing chamber comprises providing a gas in a vortex flow into the chamber. Another method of delivering gases to a substrate in a substrate processing chamber comprises providing a flow of a gas in a substantially uniform velocity across the surface of the substrate.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0012] So that the manner in which the above recited features, advantages and objects of the present invention are attained and can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings.

[0013] It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0014] Figure 1 is a schematic cross-sectional view of a prior art chamber adapted for chemical vapor deposition or for atomic layer deposition.

[0015] Figure 2 is a schematic cross-sectional view of one embodiment of a chamber including a gas delivery apparatus adapted for atomic layer deposition.

[0016] Figures 3A-C are schematic side cross-sectional simplified representations of a flow of a pulse of gas from the between the bottom surface of a covering and the surface of a substrate.

[0017] Figure 4 is a schematic cross-sectional view of another embodiment of a covering.

[0018] Figure 5 is a top cross-sectional view of one embodiment of the conical section of the covering of Figure 4.

[0019] Figure 6 is an enlarged side cross-sectional view of the conical section of the covering of Figure 5.

[0020] Figure 7 is a schematic cross-sectional view of another embodiment of the

covering of Figure 2.

[0021] Figure 8 is a top cross-sectional view of one embodiment of the conical section of the covering of Figure 7.

[0022] Figure 9 is an enlarged side cross-sectional view of the conical section of the covering of Figure 8.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

[0023] Figure 2 is a schematic side cross-sectional view of one embodiment of a chamber 200 including a gas delivery apparatus 230 adapted for atomic layer deposition. The chamber 200 comprises a chamber body 202 having sidewalls 204 and a bottom 206. An opening (not shown) in the chamber 200 provides access for a robot (not shown) to deliver and retrieve a substrate 210, such as a 200 mm or 300 mm semiconductor wafer or a glass substrate, from the chamber 200.

[0024] A substrate support 212 supports the substrate 210 in the chamber 200. The substrate support 212 is mounted to a lift motor 214 to raise and lower the substrate support 212 and a substrate 210 disposed thereon. A lift plate 216 connected to a lift motor 218 is mounted in the chamber 200 and raises and lowers pins 220 movably disposed through the substrate support 212. The pins 220 raise and lower the substrate 210 over the surface of the substrate support 212.

[0025] The substrate support 212 may be heated to heat the substrate 210 disposed thereon. For example, the substrate support 212 may be heated using an embedded heating element, such as a resistive heater, or may be heated using radiant heat, such as heating lamps. A purge ring 228 may be optionally disposed on the substrate support 212 which defines a channel which provides a purge gas to a peripheral portion of the substrate 210 to prevent deposition thereon.

[0026] A gas delivery apparatus 230 is disposed at an upper portion of the chamber body 202 to provide a gas, such as a process gas or a purge gas, to the chamber 200. A vacuum system 278 is in communication with a pumping channel 279 to evacuate any gas from the chamber 200 and to help maintain a desired pressure or a desired pressure range inside a pumping zone 255 of chamber 200.

[0027] In one embodiment, the gas delivery apparatus 230 comprises a covering 232 positioned over the substrate support 212. As shown in Figure 2, the covering is

integrated with the chamber lid. In other embodiments, the covering 232 may be separate from the chamber lid. The covering 232 further comprises a passageway 236 having an inlet 261 to provide a gas flow from one or more gas sources 240a, 240b through at least one valve 244. The valve 244 may be coupled to the inlet 261 through a channel 242. Channel 242 may be integrated or may be separate from the valve 244. The valve 244 may be adapted to provide a single or a plurality of gases from the gas sources 240a, 240b separately or together. In one embodiment, the valve 244 is coupled in close proximity or coupled directly to the covering 232 to reduce any unnecessary volume in which a gas flow must travel from the valve 244. The valve 244 may be any suitable valve. Preferably, the valve 244 is a zero dead volume valve to enable rapid flushing of the lines of the valve. A zero dead volume valve is further described in U.S. Patent 6,096,134, entitled "Liquid Delivery System," which is incorporated by reference in its entirety to the extent not inconsistent with this patent. The valve 244 may be pneumatically actuated or electrically actuated.

[0028] The bottom surface 234 of the covering 232 initially contains gases in a reaction zone 250. The term "reaction zone" as used herein is defined as the space between the substrate 210 and the bottom surface 234 of the covering 232 including the space of the passageway 236 of the covering to the valve 244 and between the edge of the substrate 210 to the most adjacent point on the bottom surface 234 of the covering 232. In one aspect, the reaction zone 250 comprises a small volume compared to conventional CVD which requires a small amount of gas to fill the reaction zone 250 for a particular process, such as for a reactant gas or a purge gas in a sequential introduction of pulses of gases in an atomic layer deposition sequence. In one embodiment, the substrate support 212 may be raised or lowered to adjust the volume of the reaction zone 250. Because a small amount of gas, whether a deposition gas or a purge gas, is necessary to be flowed into the chamber 200, the throughput is greater and the waste may be minimized due to the smaller amount of gas used reducing the cost of operation.

[0029] In one embodiment, a substantial portion of the bottom surface 234 of the covering 232 is flat. In another embodiment, as shown in Figure 2, at least a portion of the bottom surface 234 of the covering 232 is downwardly sloping. In one embodiment, the bottom surface 234 of the covering 232 is downwardly sloping to provide a substantially uniform velocity of a gas flow from passageway 236 across the

surface of the substrate 210.

[0030] Not wishing to be bound by theory, Figure 3A-C are schematic side cross-sectional simplified representations of a flow of a pulse 310 of gas from the passageway 236 between the bottom surface 234 of covering 232 and the surface of a substrate 210. In Figure 3A, a pulse 310 of gas is introduced into the reaction zone 250 through the passageway 236. Figure 3B shows the pulse 310 of gas as it travels away from the passageway 236. Figure 3C shows the pulse 310 of gas as it travels further away from the passageway 236. The pulse 310 of gases, as shown in Figure 3B and Figure 3C, travels across the substrate 210 as an expanding ring. The velocity of the pulse 310 is equal to the flow over the cross-sectional area in which the flow is traveling. In other words, the velocity of a pulse 310 of gas is inversely proportional to the outer side surface area ( $h \times 2 \pi r$ ) of the ring which represents the position of a pulse 310 of gas at a particular time. In other words, the velocity of a pulse 310 of gas is inversely proportional to the height "h" of the ring and the radius "r" of the ring. Comparing the velocity of the pulse in Figure 3B versus the velocity in Figure 3C, the radius of the ring increases from Figure 3B to Figure 3C while the height of the ring decreases from Figure 3B to Figure C. The factor of a larger radius alone would indicate that the velocity of the pulse is slower in Figure 3C than in Figure 3B. The factor of a smaller height alone would indicate that the velocity of the pulse is faster in Figure 3C than in Figure 3B. Therefore, the slope of the bottom surface 234 of the covering 232 may be adjusted so that the combination of factors of the height and the radius of the ring produces a pulse velocity that is substantially uniform. In one embodiment, a substantially uniform pulse velocity comprises a ratio of the maximum velocity over the minimum velocity of the pulse as it travels between the downwardly sloping surface 234 and the substrate 210 is less than about 4.0, preferably less than about 2.0.

[0031] Referring to Figure 2 and Figures 3A-C, the covering 232 may have a lip 239 at an outer portion of the bottom surface of the covering adjacent a peripheral portion of the substrate 210 to act as a pressure control. The lip 239 may comprise any downwardly extending protrusion. In one aspect, the lip 239 helps isolate the reaction zone 250 from the non-uniform pressure in the pumping zone 255 (Figure 2) which helps to provide a more uniform flow of gas through the reaction zone 250.

[0032] Referring to Figure 2, the covering 232 may be made of aluminum, nickel-plated

aluminum, nickel, stainless steel, or other suitable materials. Referring to Figure 2, the covering 232 may include cooling elements or heating elements depending on the particular gas being delivered therethrough. One example of cooling elements are water channels 238 formed in the covering 232. Controlling the temperature of the covering 232 may be used to prevent gas decomposition, deposition, or condensation on the covering 232 and to aid in uniform deposition.

[0033] In one embodiment, the bottom surface 234 of the covering 232 comprises a mirror polished surface having an average roughness between about 4.0 to about 8.0 to help produce a more laminar flow of a gas along the bottom surface 234 of the covering 232. In another embodiment, the inner surface of the channel 242 is electropolished to help produce a more laminar flow of a gas therethrough.

[0034] A control unit 280, such as a programmed personal computer, work station computer, and the like, may be coupled to the chamber 200 to control processing conditions. For example, the control unit 280, may be configured to control flow of various process gases and purge gases through gas sources 240a, 240b and through the valve 244 during different stages of a substrate process sequence. Illustratively, the control unit 280 comprises a central processing unit (CPU) 282, support circuitry 284, and memory 286 containing associated control software 283. The control unit 280 may be one of any form of general purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. The CPU 282 may use any suitable memory 286, such as random access memory, read only memory, floppy disk drive, hard disk, or any other form of digital storage, local or remote. Various support circuits may be coupled to the CPU 282 for supporting the chamber 200. The control unit 280 may be coupled to another controller (not shown) that is located adjacent individual chamber components, such as a programmable logic controller for an electrically controlled valve. Bi-directional communications between the control unit 280 and various other components of the chamber 200 are handled through numerous signal cables collectively referred to as signal buses 288, some of which are illustrated in FIG. 2. In addition to control of process gases and purge gases from gas sources 240a, 240b and through the valve 244, the control unit 280 may be configured to be responsible for automated control of other activities used in wafer processing--such as wafer transport, temperature control, chamber evacuation, among other activities, some of which are described elsewhere herein.

[0035] Figure 4 is a schematic cross-sectional view of another embodiment of the covering 232 of Figure 2 in which the passageway 236 (Figure 2) comprises a conical section 460. In one embodiment, the channel 242 is not pointed directly downward but pointed horizontally, angled upwardly, or angled downwardly to reduce the turbulent flow of the gas due to the sudden injection of the gas into the passageway 236 or conical section 460.

[0036] Figure 5 is a top cross-sectional view of one embodiment of the conical section 460 of the covering 232 of Figure 4. In one embodiment, the channel 242 is positioned at an angle  $\alpha$  from the center line 502 of the channel 242 and from a radius line 504 from the center of the conical section 260 to the channel 242 to inject a gas flow in a circular direction in the conical section 460 as shown by arrow 510. The channel 242 may be angled horizontally, angled upwardly, or angled downwardly.

[0037] Not wishing to be bound by theory, Figure 6 is an enlarged side cross-sectional view of the conical section 460 of the covering 232 of Figure 5 illustrating the flow of a gas therethrough. Because the chamber is under a low pressure, injection of a gas flow at an angle  $\alpha$  causes the gas to flow in a more laminar flow in a "vortex" or "spiral" pattern through the conical section 460 as shown by arrow 602. In one aspect, the vortex flow helps to establish a more efficient purge or sweep through the internal area of the conical section 460 due to the vortex flow pattern. In one embodiment, the height 610 of the conical section 460 between the gas inlet 261 and the top of the substrate 210 disposed on the substrate support 212 is made high enough that the "vortex" flow dissipates to a downwardly flow as shown by arrows 604 which aids in a more uniform flow of gases across the substrate as a spiral flow across the surface of the substrate 210 may not be desirable. In one embodiment the height of the conical section is about 3 inches or more. The "vortex" flow 602 and the downwardly flow 604 efficiently purges the reaction zone due to the laminar flow of through the entire volume of the covering. The flow of gases across the surface of the substrate then proceeds in a manner as depicted in Figures 3A-3C.

[0038] Referring to Figure 4, the channel 242 or a portion of the channel may be gradually expanding to help produce a more laminar flow of gas therethrough by helping to reduce the jet speed in which a flow of gas is initially injected. In another aspect, a gradually expanding channel helps to control the temperature and flow velocity of a gas due to the non-adiabatic expansion of the gas. For example, the

channel may comprise a plurality of channels coupled together in which each channel has a slightly larger diameter than an adjacent channel.

[0039] Figure 7 is a schematic cross-sectional view of another embodiment of the covering 232 of Figure 2 in which the conical section 460 has a plurality of gas inlets 261a, 261b coupled to a single or a plurality of gas source(s) or gas mixture source(s) 240a, 240b, 241a, 241b through a single or a plurality of valves 244a, 244b. Each valve 244a, 244b may be adapted to provide a gas or gas mixture from the gas sources 240a, 240b, 241a, 241b separately or together. The valves 244a, 244b may be provided a gas or gas mixture separately or together.

[0040] Figure 8 is a top cross-sectional view of one embodiment of the conical section 460 of the covering 232 of Figure 7 as two gas flows are injected at the same time into the conical section 460. In one embodiment, the channels 242a, 242b are positioned at an angle to inject a gas flow in a circular direction in the conical section 460 as shown by arrow 710. Each channel 242 may be angled horizontally, angled upwardly, or angled downwardly. In one embodiment as shown, the channels 242a, 242b and the corresponding inlets 261a, 261b are spaced out from each other and direct a flow in the same circular direction (i.e. clockwise or counter-clockwise) to provide a more uniform gas flow.

[0041] Not wishing to be bound by theory, Figure 9 is an enlarged side cross-sectional view of the conical section 460 of the covering 232 of Figure 8. Because the chamber is under a low pressure, injection of a gas flow at an angle  $\alpha$  causes the gas to flow in a "vortex" or "spiral" flow through the conical section 460 as shown by arrows 902a, 902b. Injecting a plurality of gas flows in a vortex pattern reduces the likelihood that the gas flow does not sufficiently sweep a particular surface. Furthermore, a plurality of gas flows helps provide a more uniform gas flow across the surface of the substrate 210.

[0042] Figures 7-9 show a chamber adapted to provide two gas flows. In other embodiments, the chamber may be adapted to provide three or more gas flows. The gas delivery 230 of Figures 2-9 has been described above as being integrated with the chamber lid 232. In other embodiments, the gas delivery apparatus may be separate from the chamber lid. For example, the gas delivery apparatus may be any covering disposed over the substrate support 212 to delineating a reaction zone 250 which lowers the volume in which a gas must flow during substrate processing. In other

embodiments, instead or in conjunction with the substrate support 212, the covering may be adapted to move up and down to adjust the volume of the reaction zone 250.

[0043] Embodiments of chamber 200 with gas delivery apparatus 230 as described in Figures 2-9 may be used to advantage to implement atomic layer deposition processes of elements, which include but is not limited to, tantalum, titanium, tungsten, and copper, or to implement atomic layer deposition of compounds, which include but is not limited to tantalum nitride, tantalum silicon nitride, titanium nitride, titanium silicon nitride, tungsten nitride, and tungsten silicon nitride. Embodiments of chamber 200 with gas delivery apparatus 230 as described in Figure 2-9 may also be used to advantage to implement chemical vapor deposition of various materials.

[0044] For clarity reasons, deposition of a layer by atomic layer deposition will be described in more detail in reference to the atomic layer deposition of a tantalum nitride layer utilizing the chamber 200 as described in Figures 7-9. In one aspect, atomic layer deposition of a tantalum nitride barrier layer comprises sequentially providing pulses of a tantalum containing compound and pulses of a nitrogen containing compound to the process chamber 200 in which each pulse is separated by a flow of a purge gas and/or chamber evacuation to remove any excess reactants to prevent gas phase reactions of the tantalum containing compound with the nitrogen containing compound and to remove any reaction by-products. Sequentially providing a tantalum containing compound and a nitrogen containing compound may result in the alternating chemisorption of monolayers of a tantalum containing compound and of monolayers of a nitrogen containing compound to form a monolayer of tantalum nitride on a substrate structure for each cycle of pulses. The term substrate structure is used to refer to the substrate as well as other material layers formed thereover, such as a dielectric layer.

[0045] It is believed that the chemisorption processes used to absorb the monolayer of the reactants, such as the tantalum containing compound and the nitrogen containing compound, are self-limiting in that only one monolayer may be chemisorbed onto the surface of the substrate structure during a given pulse because the surface of the substrate structure has a finite number of sites for chemisorbing the reactants. Once the finite number of sites are occupied by the reactants, such as the tantalum containing compound or the nitrogen containing compound, further chemisorption of the reactants will be blocked. The cycle may be repeated to a desired thickness of the tantalum nitride layer.

[0046] Pulses of a tantalum containing compound, such as pentadimethylamino-tantalum (PDMAT; Ta(NMe<sub>2</sub>)<sub>5</sub>), may be introduced by gas source 240a through valve 244a. The tantalum containing compound may be provided with the aid of a carrier gas, which includes, but is not limited to, helium (He), argon (Ar), nitrogen (N<sub>2</sub>), hydrogen (H<sub>2</sub>), and combinations thereof. Pulses of a nitrogen containing compound, such as ammonia, may be introduced by gas source 241 through valve 244b. A carrier gas may also be used to help deliver the nitrogen containing compound. A purge gas, such as argon, may be introduced by gas source 240b through valve 244a and by gas source 241b through valve 244b. In one aspect, the flow of purge gas may be continuously provided by gas sources 240b, 241b through the valve to act as a purge gas between the pulses of the tantalum containing compound and of the nitrogen containing compound and to act as a carrier gas during the pulses of the tantalum containing compound and of the nitrogen containing compound. In one aspect, the purge gas may be provided by the plurality of valves 244a, 244b through the plurality of inlets 261a, 261b to provide a more complete purge of the reaction zone 250 and to provide a purge of the channels 242a, 242b. In one aspect, a tantalum containing compound or a nitrogen containing compound may be provided by one valve through one inlet since uniformity of flow of a reactant, such as a tantalum containing compound or a nitrogen containing compound, is not as critical as uniformity of the purge gas due to the self-limiting chemisorption process on the surface of substrate structures of the reactants. In other embodiments, a purge gas may be provided in pulses. In other embodiments, a purge gas may be provided in more or less than two gas flows. In other embodiments, a tantalum containing gas may be provided in more than a single gas flow (i.e. two or more gas flows). In other embodiments, a nitrogen containing may be provided in more than a single gas flow (i.e. two or more gas flows).

[0047] Other examples of tantalum containing compounds, include, but are not limited to, other organo-metallic precursors or derivatives thereof, such as pentaethylmethylamino-tantalum (PEMAT; Ta[N(C<sub>2</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub>), pentadiethylamino-tantalum (PDEAT; Ta(NEt<sub>2</sub>)<sub>5</sub>), and any and all of derivatives of PEMAT, PDEAT, or PDMAT. Other tantalum containing compounds include without limitation TBTDET (Ta(NEt<sub>2</sub>)<sub>3</sub>NC<sub>4</sub>H<sub>9</sub> or C<sub>16</sub>H<sub>39</sub>N<sub>4</sub>Ta) and tantalum halides, for example TaX<sub>5</sub> where X is fluorine (F), bromine (Br) or chlorine (Cl), and derivatives thereof. Other nitrogen containing compounds may be used which include, but are not limited to, N<sub>x</sub>H<sub>y</sub> with x

and  $y$  being integers (e.g., hydrazine ( $N_2H_4$ )), dimethyl hydrazine ( $(CH_3)_2N_2H_2$ ), t-butylhydrazine ( $C_4H_9N_2H_3$ ) phenylhydrazine ( $C_6H_5N_2H_3$ ), other hydrazine derivatives, a nitrogen plasma source (e.g.,  $N_2$ ,  $N_2/H_2$ ,  $NH_3$ , or a  $N_2H_4$  plasma), 2,2'-azoisobutane ( $(CH_3)_2C_2N_2$ ), ethylazide ( $C_2H_5N_3$ ), and other suitable gases. Other examples of purge gases include, but are not limited to, helium (He), nitrogen ( $N_2$ ), hydrogen ( $H_2$ ), other gases, and combinations thereof.

[0048] The tantalum nitride layer formation is described as starting with the chemisorption of a monolayer of a tantalum containing compound on the substrate followed by a monolayer of a nitrogen containing compound. Alternatively, the tantalum nitride layer formation may start with the chemisorption of a monolayer of a nitrogen containing compound on the substrate followed by a monolayer of the tantalum containing compound. Furthermore, in other embodiments, a pump evacuation alone between pulses of reactant gases may be used to prevent mixing of the reactant gases.

[0049] The time duration for each pulse of the tantalum containing compound, the time duration for each pulse of the nitrogen containing compound, and the duration of the purge gas between pulses of the reactants are variable and depend on the volume capacity of a deposition chamber employed as well as a vacuum system coupled thereto. For example, (1) a lower chamber pressure of a gas will require a longer pulse time; (2) a lower gas flow rate will require a longer time for chamber pressure to rise and stabilize requiring a longer pulse time; and (3) a large-volume chamber will take longer to fill, longer for chamber pressure to stabilize thus requiring a longer pulse time. Similarly, time between each pulse is also variable and depends on volume capacity of the process chamber as well as the vacuum system coupled thereto. In general, the time duration of a pulse of the tantalum containing compound or the nitrogen containing compound should be long enough for chemisorption of a monolayer of the compound. In general, the duration of the purge gas and/or pump evacuation should be long enough to remove the reaction by-products and/or any residual materials remaining in the process chamber.

[0050] Generally, a pulse time of about 1.0 second or less for a tantalum containing compound and a pulse time of about 1.0 second or less for a nitrogen containing compound are typically sufficient to chemisorb alternating monolayers on a substrate structure. A time of about 1.0 second or less between pulses of the tantalum

containing compound and the nitrogen containing compound is typically sufficient for the purge gas, whether a continuous purge gas or a pulse of a purge gas, to remove reaction by-products as well as any residual materials remaining in the process chamber. Of course, a longer pulse time of the reactants may be used to ensure chemisorption of the tantalum containing compound and the nitrogen containing compound and a longer time between pulses of the reactants may be used to ensure removal of the reaction by-products.

[0051] During atomic layer deposition, the substrate 210 may be maintained approximately below a thermal decomposition temperature of a selected tantalum containing compound. An exemplary heater temperature range to be used with tantalum containing compounds identified herein is approximately between about 20°C and about 500°C at a chamber pressure less than about 100 torr, preferably less than 50 torr. When the tantalum containing gas is PDMAT, the heater temperature is preferably between about 100°C and about 300°C, more preferably between about 175°C and 250°C. In other embodiments, it should be understood that other temperatures may be used. For example, a temperature above a thermal decomposition temperature may be used. However, the temperature should be selected so that more than 50 percent of the deposition activity is by chemisorption processes. In another example, a temperature above a thermal decomposition temperature may be used in which the amount of decomposition during each precursor deposition is limited so that the growth mode will be similar to an atomic layer deposition growth mode.

[0052] One exemplary process of depositing a tantalum nitride layer by atomic layer deposition in the process chamber 200 of Figure 7-9, comprises providing pulses of pentadimethylamino-tantalum (PDMAT) from gas source 240a at a flow rate between about 100 sccm and about 1000 sccm through valve 244a for a time period of about 1.0 second or less. A pulse time of the valve 244a may be less than 0.5 seconds, less than about 0.1 seconds, or even less than about 0.05 due the smaller volume of the reaction zone 250. Pulses of ammonia may be provided from gas source 241a at a flow rate between about 100 sccm and about 1000 sccm for a time period of about 1.0 second or less. A pulse time of the valve 244b may be less than about 0.5 seconds, less than about 0.1 seconds, or even less than about 0.05 seconds due to a smaller volume of the reaction zone 250. An argon purge gas at a flow rate between about

100 sccm and about 1000 sccm may be continuously provided from gas source 240b and 241b. The time between pulses of the tantalum containing compound and the nitrogen containing compound may be about 1.0 second or less. The time between pulses of the tantalum containing compound and the nitrogen containing compound may be less than about 0.5 seconds, may be less than about 0.1 seconds, or even less than about 0.07 seconds due to the smaller volume of the reaction zone 250. The heater temperature preferably is maintained between about 100°C and about 300°C at a chamber pressure between about 1.0 and about 5.0 torr. This process provides a tantalum nitride layer in a thickness between about 0.5 Å and about 1.0 Å per cycle. The alternating sequence may be repeated until a desired thickness is achieved.

[0053] In one embodiment, the layer, such as a tantalum nitride layer, is deposited to a sidewall coverage of about 50 Å or less. In another embodiment, the layer is deposited to a sidewall coverage of about 20 Å or less. In still another embodiment, the layer is deposited to a sidewall coverage of about 10 Å or less. A tantalum nitride layer with a thickness of about 10 Å or less is believed to be a sufficient thickness in the application as a barrier layer to prevent copper diffusion. In one aspect, a thin barrier layer may be used to advantage in filling sub-micron and smaller features having high aspect ratios. Of course, a layer having a sidewall coverage of greater than 50 Å may be used.

[0054] Embodiments of atomic layer deposition have been described above as chemisorption of a monolayer of reactants on a substrate. The present invention also includes embodiments in which the reactants are deposited to more or less than a monolayer. The present invention also includes embodiments in which the reactants are not deposited in a self-limiting manner. The present invention also includes embodiments in which deposition occurs in mainly a chemical vapor deposition process in which the reactants are delivered sequentially or simultaneously.

[0055] Embodiments of atomic layer deposition have been described above as the deposition of the binary compound of tantalum nitride utilizing pulses of two reactants. In the deposition of other elements or compounds, pulses of two or more reactants may also be used. For example, for the deposition of a tertiary compound, such as TaSiN, pulses of three reactants may be used. The pulse of three reactants may be delivered in a variety of sequences. For example, pulses may be delivered sequentially (i.e. A → B → C), the pulses may be delivered in which two pulses at least partially overlap with one another (i.e. A → B+C or A +B → A+C), or any other

sequence (i.e., A -> B -> A -> C) .

[0056] While foregoing is directed to the preferred embodiment of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

**Claims:**

1. A gas containment apparatus, comprising:  
a covering having a passageway adapted for introduction of a gas flow and  
having a bottom surface sized and shaped to substantially cover a substrate disposed  
on a substrate support, the covering adapted to be positioned adjacent a substrate  
defining a reaction zone between the bottom surface of the covering and the substrate.

2. A gas delivery apparatus, comprising:  
a covering comprising a conical section and a bottom surface size and shaped  
to substantially cover a substrate disposed on a substrate support, the conical section  
having at least one gas inlet adapted to receive a gas flow, the covering adapted to be  
positioned adjacent a substrate defining a reaction zone between the covering and the  
substrate.

3. A gas delivery apparatus, comprising:  
a covering comprising a conical section and a bottom surface size and shaped  
to substantially cover a substrate disposed on a substrate support, the conical section  
having at least one gas inlet adapted to receive a gas flow, the covering adapted to be  
positioned adjacent a substrate defining a reaction zone between the covering and the  
substrate; and

    a channel coupled to each gas inlet and adapted to provide the gas flow, the  
channel pointed in a direction selected from the group consisting of horizontally, angled  
upwardly, and angled downwardly.

4. A gas delivery apparatus, comprising:  
a covering comprising a conical section and a bottom surface size and shaped  
to substantially cover a substrate disposed on a substrate support, the conical section  
having one or more gas inlets adapted to receive a gas flow, the covering adapted to  
be positioned adjacent a substrate defining a reaction zone between the covering and  
the substrate; and

    a channel coupled to each gas inlet and adapted to provide the gas flow, the  
channel pointed in a direction selected from the group consisting of horizontally, angled  
upwardly, and angled downwardly and pointed at an angle from the center of the

conical section.

5. A method of depositing a material layer over a substrate structure comprising providing at least one cycle of gases, the at least one cycle comprising:

providing a continuous flow of a purge gas; and

providing alternating pulses of at least two reactants;

wherein the continuous flow of a purge gas acts as a carrier gas during the pulses of the reactants.

6. A method of depositing a material layer over a substrate structure comprising providing at least one cycle of gases, the at least one cycle comprising:

providing a first continuous flow of a purge gas and pulses of a first reactant through a first channel; and

providing a second continuous flow of a purge gas and pulses of a second reactant through a second channel, wherein the pulses of the first reactant and pulses of the second reactant are alternating and wherein the first and second continuous flows of the purge gas act as a carrier gas during the pulses of the first and the second reactants.

7. A method of delivering gases to a substrate in a substrate processing chamber; comprising:

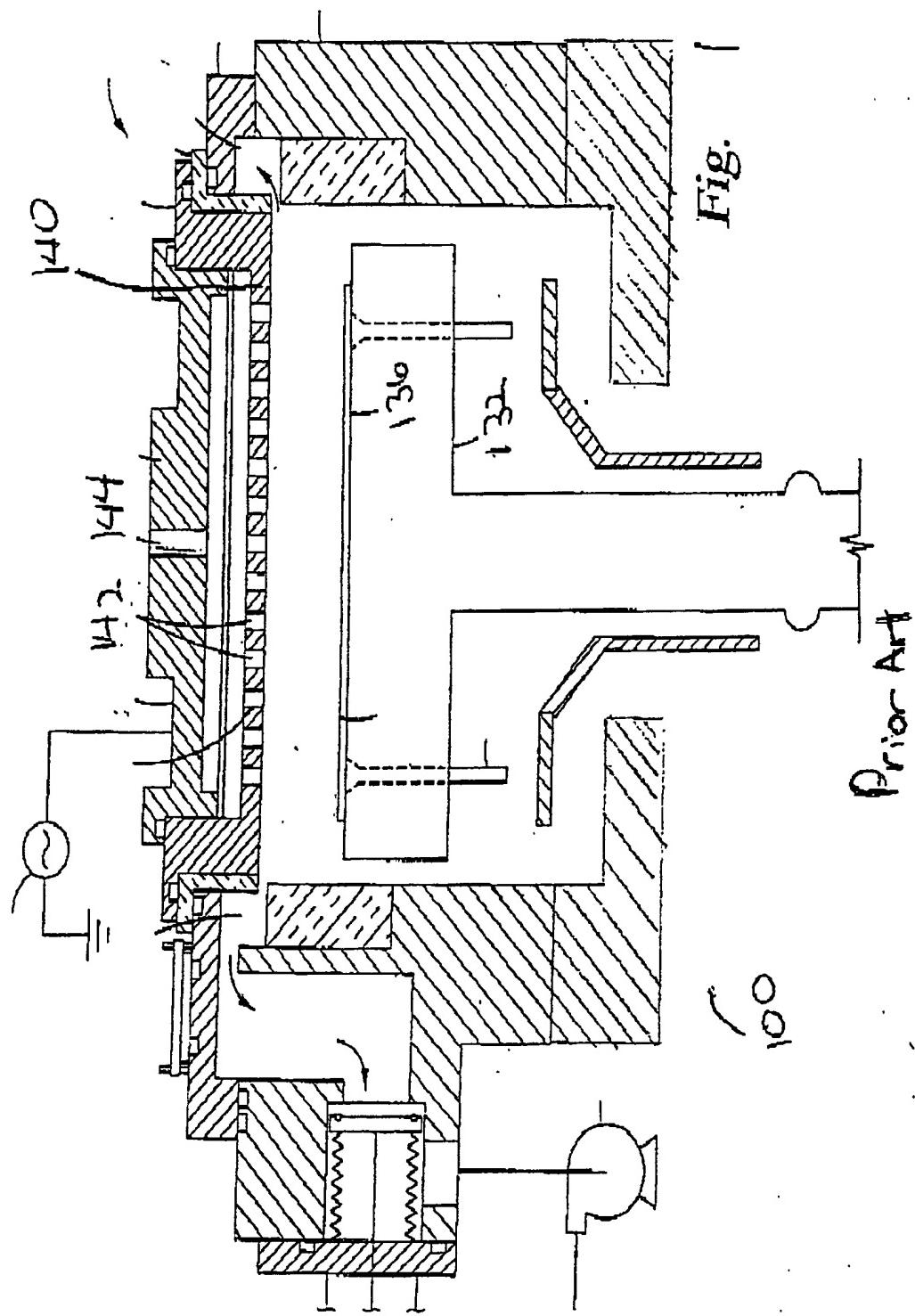
providing a gas in a vortex flow into the chamber.

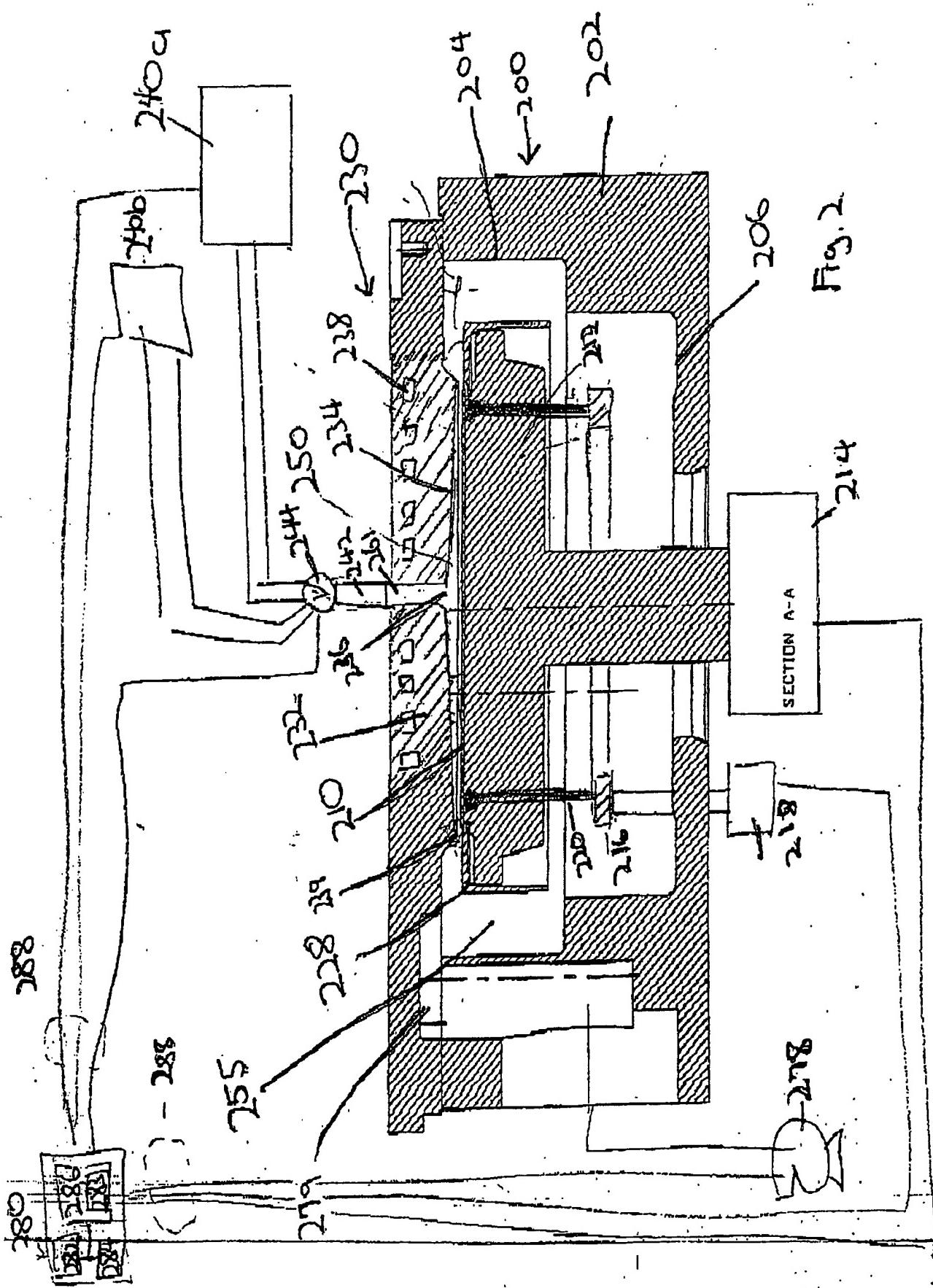
8. A method of delivering gases to a substrate in a substrate processing chamber, comprising providing a flow of a gas in a substantially uniform velocity across the surface of the substrate.

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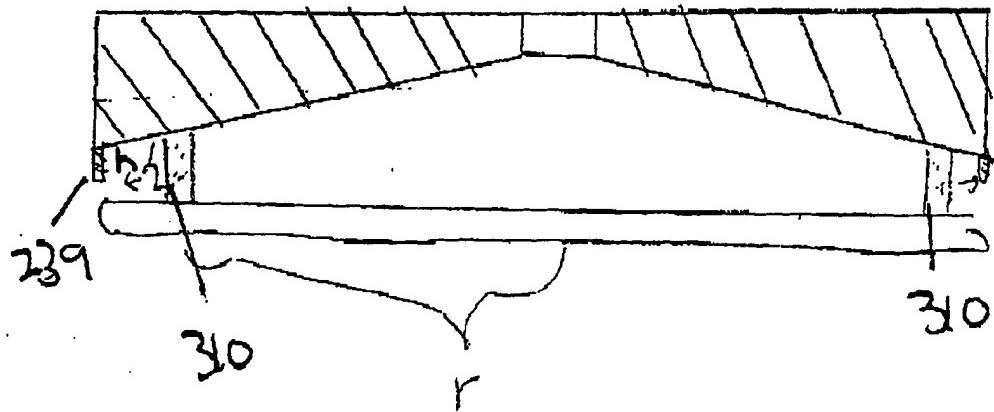
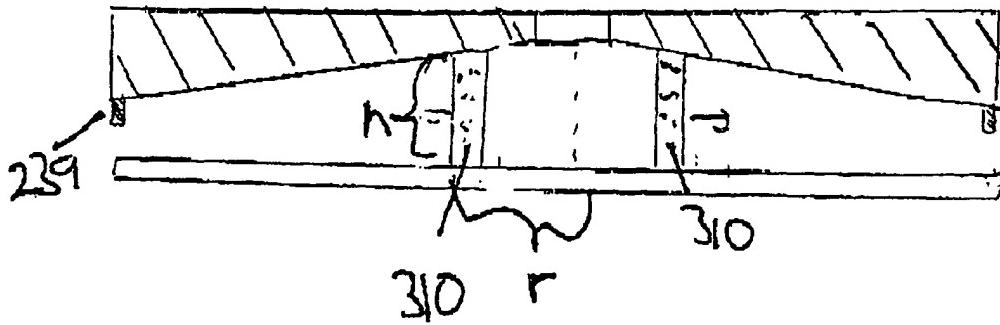
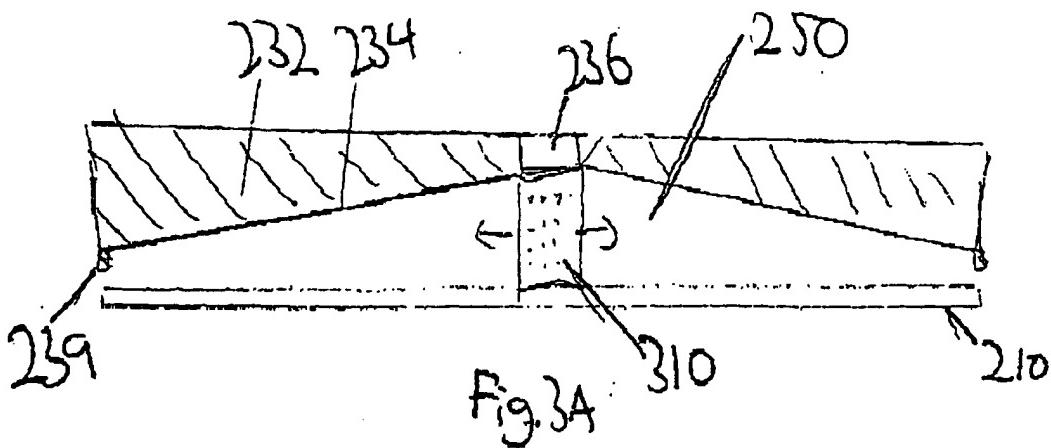
## ABSTRACT OF THE DISCLOSURE

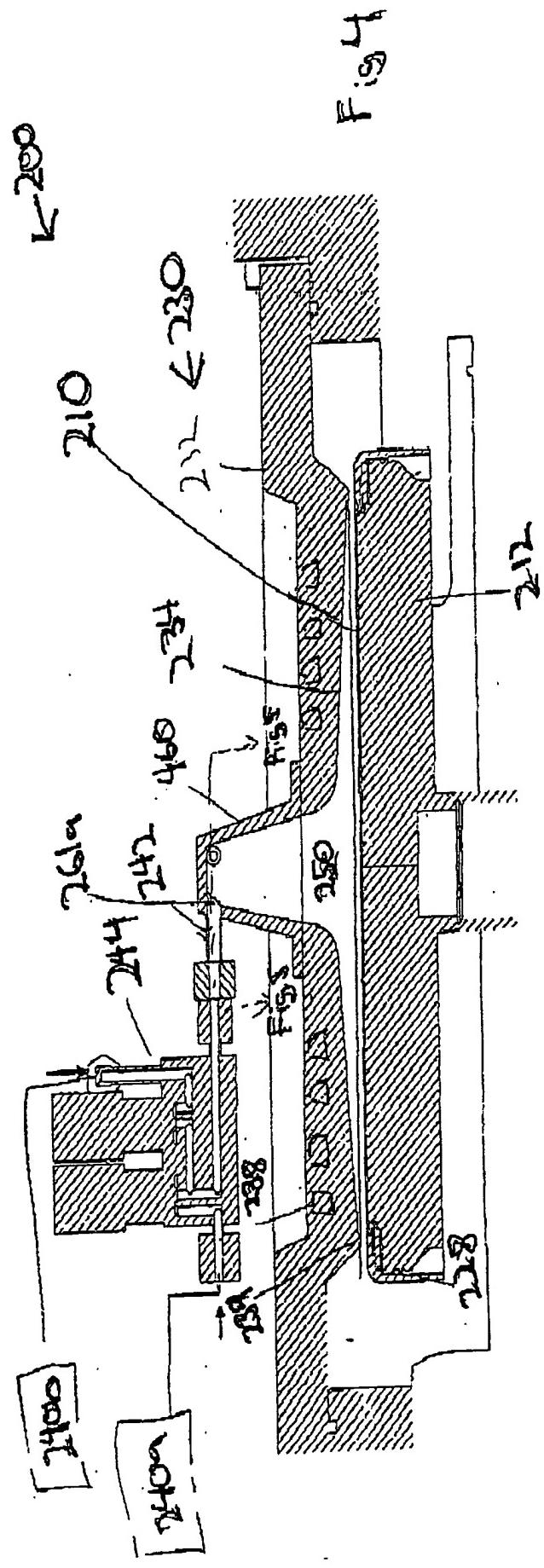
[0057] An improved gas delivery apparatus adapted for atomic layer deposition is provided. One embodiment of the gas delivery apparatus comprises a covering having a passageway adapted for introduction of a gas flow and having a bottom surface sized and shaped to substantially cover a substrate disposed on a substrate support. The covering is adapted to be positioned adjacent a substrate defining a reaction zone between the bottom surface of the covering and the substrate. In one embodiment, the passageway comprises a conical section having at least one gas inlet adapted to receive a gas flow. In another embodiment, a channel is coupled to each gas inlet of the conical section and is adapted to provide a gas flow. The channel may be pointed horizontally, angled upwardly, or angled downwardly and may be further pointed at an angle from the center of the conical section. One embodiment of a method of depositing a material layer over a substrate structure comprises providing at least one cycle of gases. One embodiment of a cycle of gases comprises providing a continuous flow of a purge gas and providing alternating pulses of at least two reactants. Another embodiment of a cycle of gases comprises providing a first continuous flow of a purge gas and pulses of a first reactant through a first channel and providing a second continuous flow of a purge gas and pulses of a second reactant through a second channel. One embodiment of a method of delivering gases to a substrate comprises providing a gas in a vortex flow into the chamber. Another method of delivering gases to a substrate in a substrate processing chamber comprises providing a flow of a gas in a substantially uniform velocity across the surface of the substrate.





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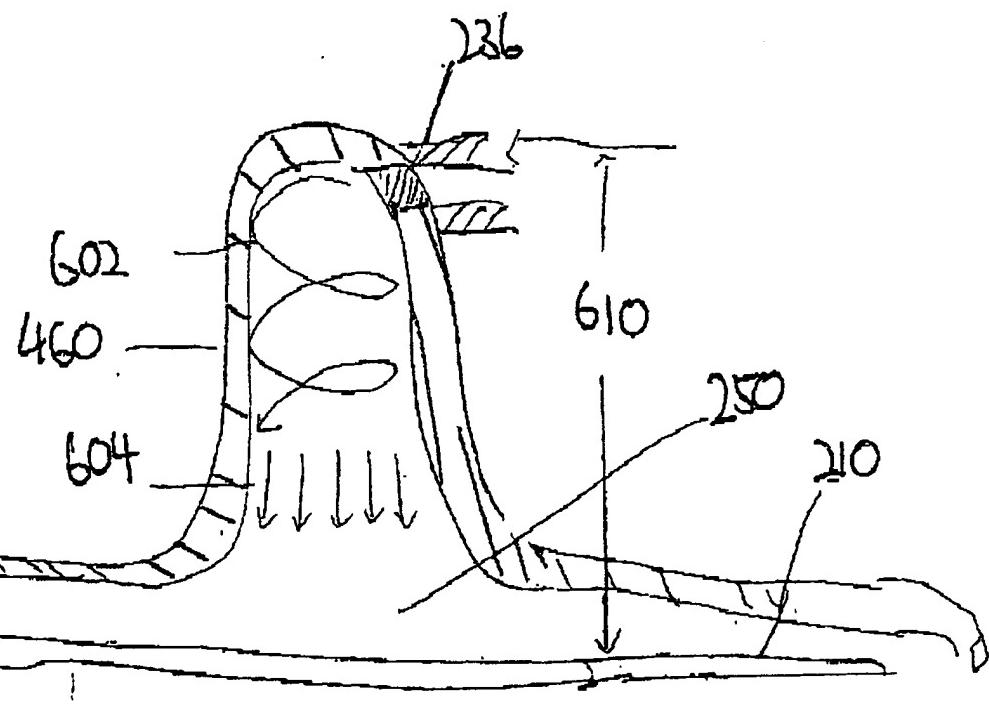
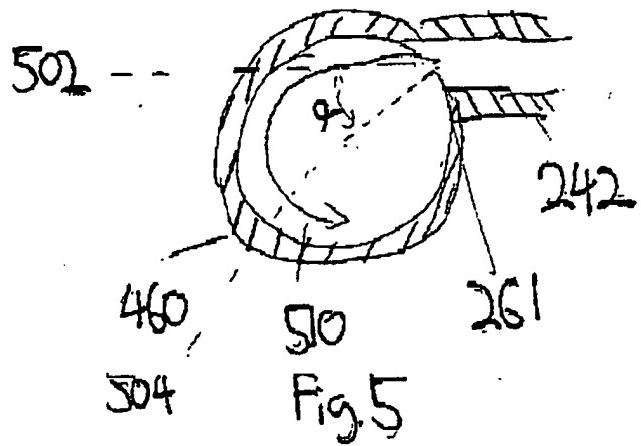
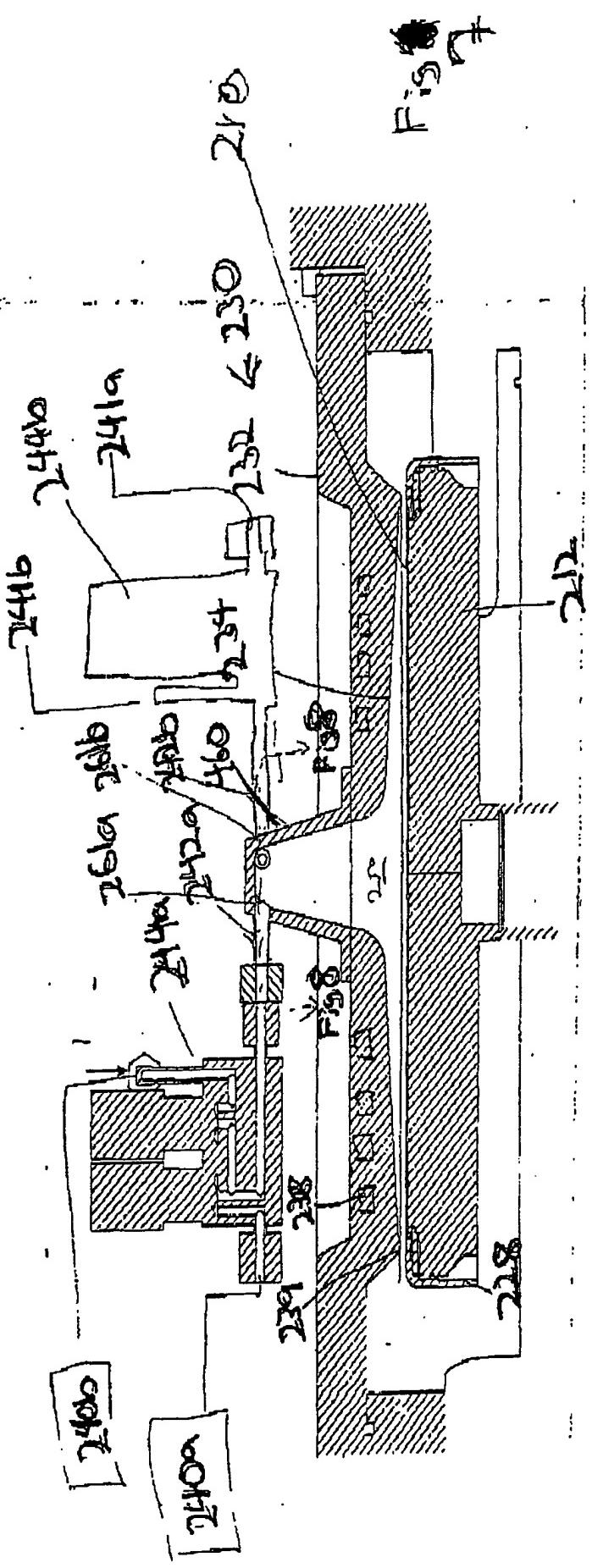
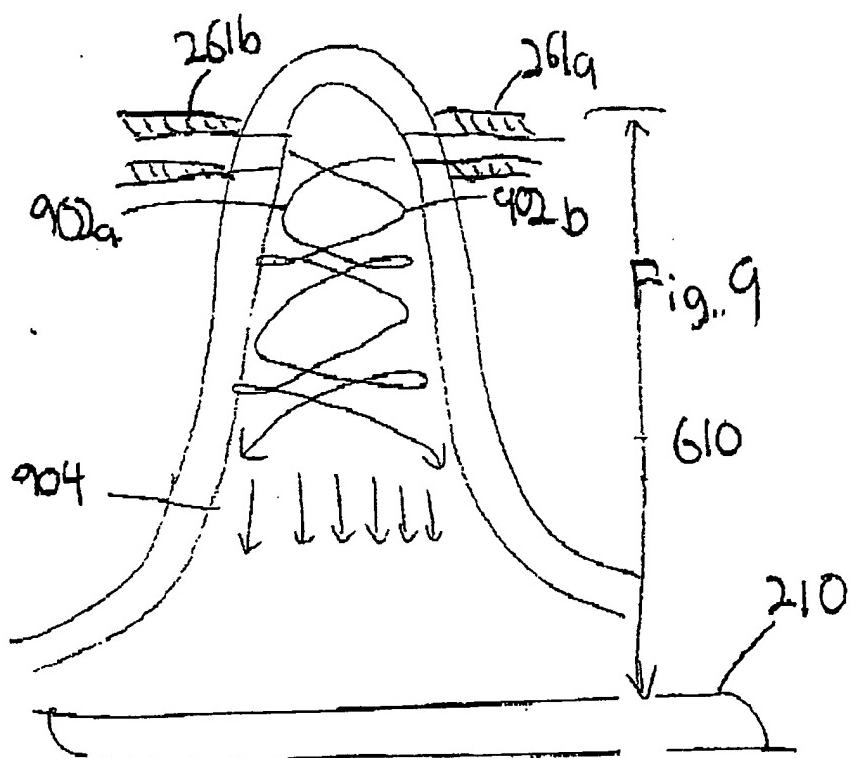
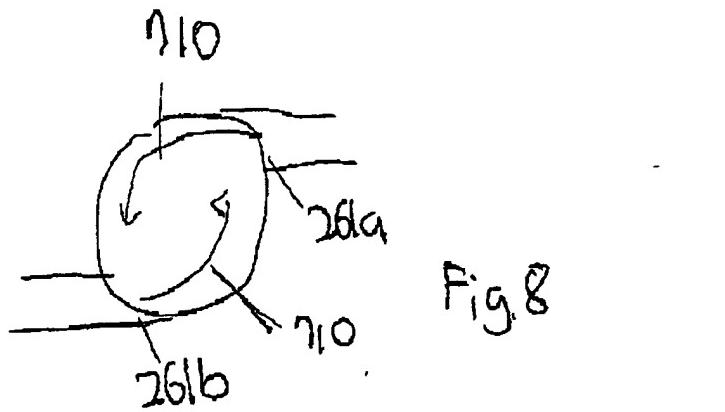


Fig. 6







# ALD TaN As Cu Barrier

Ling Chen  
Integrated Cu Barrier Seed  
CPI

Oct, 2001



CONFIDENTIAL

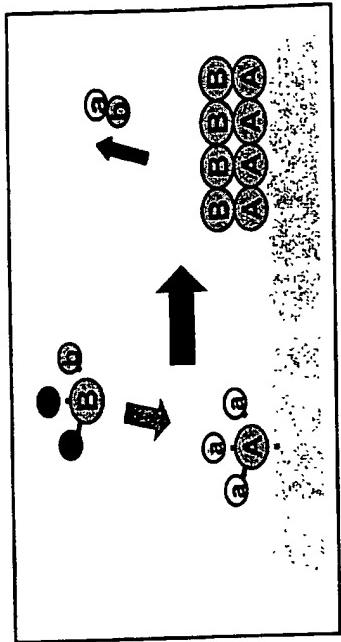
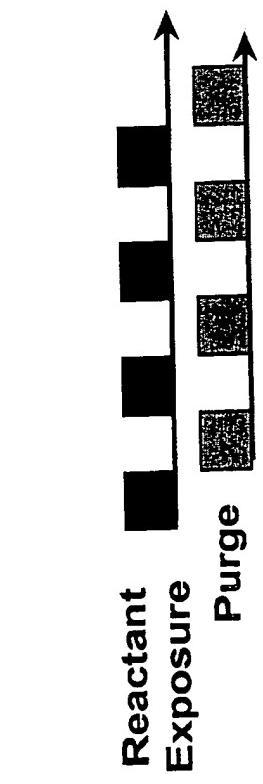
# ALD TaN Cu Barrier

- **OBJECTIVE:**
  - Develop thin TaN films (~ 10Å) for advanced Cu barrier applications
- **ISSUES:**
  - Ta-containing precursor selection and quality control
  - ALD TaN process development
  - Minimum film thickness for sufficient barrier property
  - Electrical properties of the ALD films (Via R, EM, etc)
  - Low k integration
  - Throughput



# Atomic Layer Deposition Advantages

Aa + Bb --> AB + ab↑



- Alternative introduction of two different precursors offers good uniformity control for thin films over large wafer size, 3%, 1 sigma
- Effective barrier for Cu and dielectrics
  - pin hole free
  - smooth morphology
- Excellent Thickness control for thin film <20Å for <100nm technology node
- applications
- 100% Conformal step coverage
- Wide process window
- Lower deposition temperature < 300C
- ALD TaN passed initial via resistance, and barrier performance for <20Å
- Integration with low k dielectric films, and Cu wire module ongoing

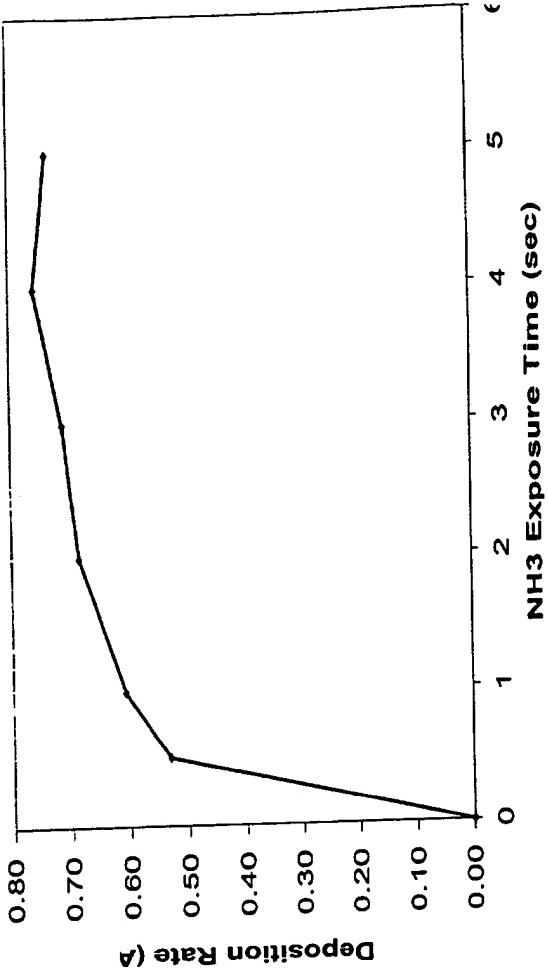
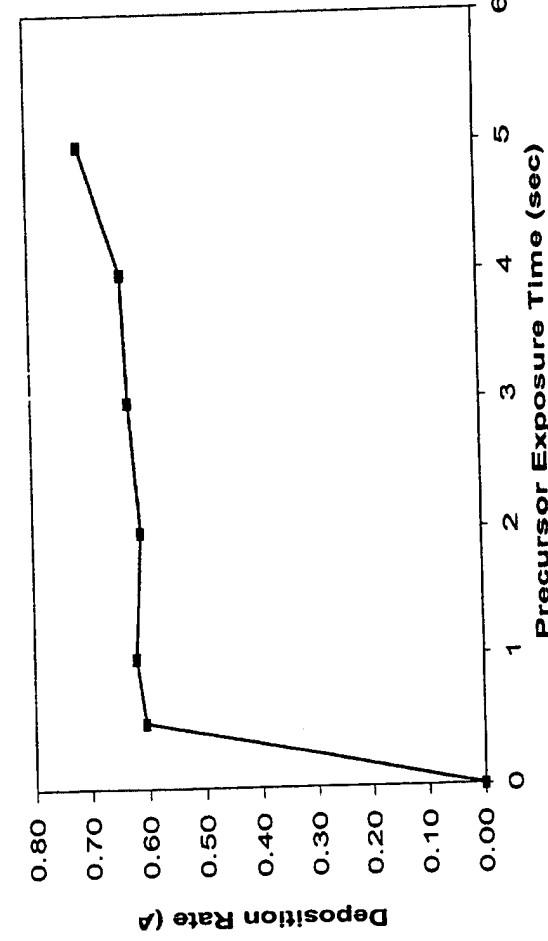
# Available Ta-Containing Precursors

## Selection Criteria:

1. Chemical stability
2. Vapor pressure
3. Immediately availability
4. Halogen-free chemistry

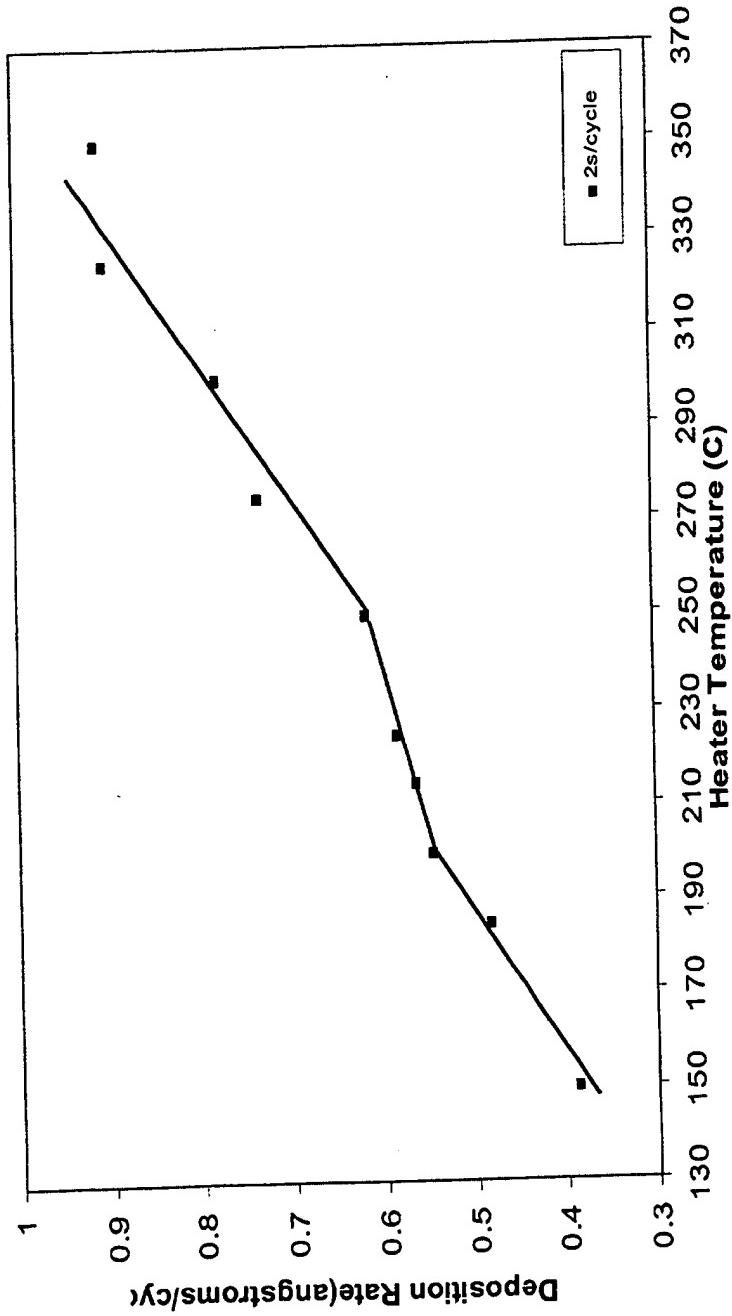


# Precursor Exposure Time Study



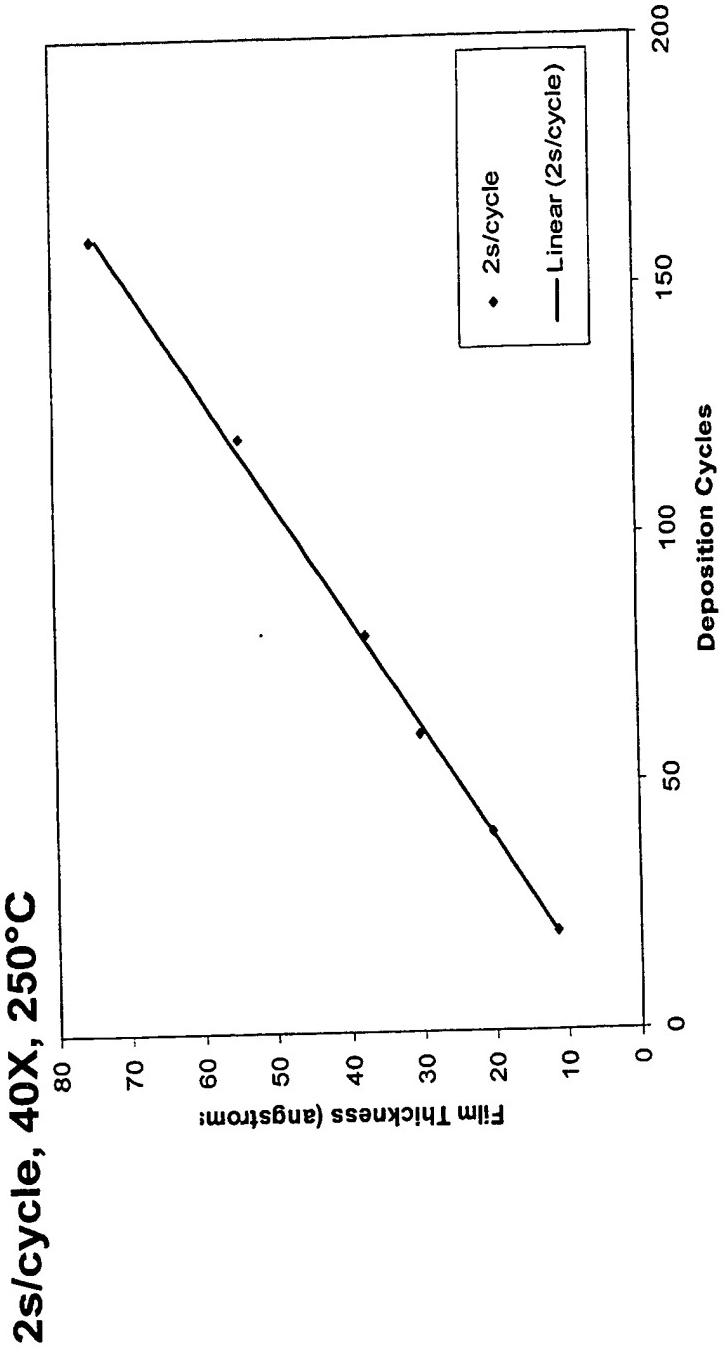
- Sub-second of exposure time for both precursor and NH<sub>3</sub> is enough

# Temperature Window



- The ALD TaN process temperature window is 200°C to 250°C

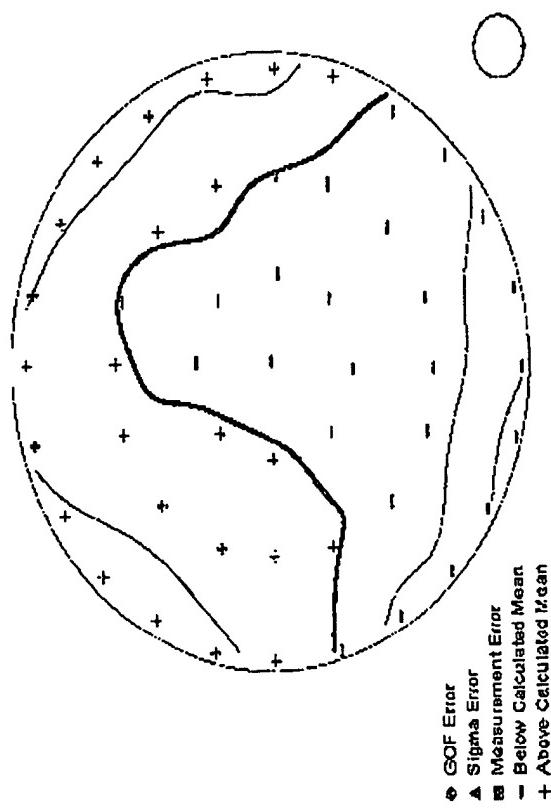
# ALD TaN Thickness Control



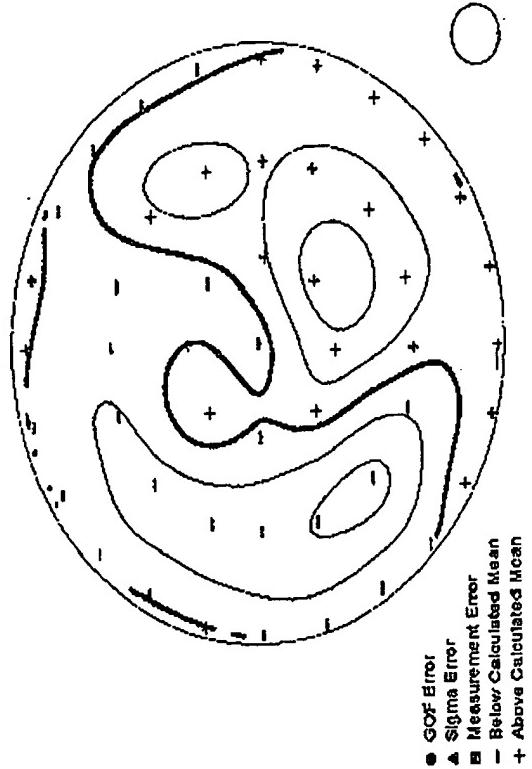
- ALD TaN film thickness is linearly proportional to deposition cycles.
- Accurate thickness control is achievable.

# ALD TaN Thickness Uniformity

TCI SEMICONDUCTOR MANUFACTURING



$10\text{ \AA}$   
 $1.8\%, 1\sigma$



$100\text{ \AA}$   
 $2.1\%, 1\sigma$



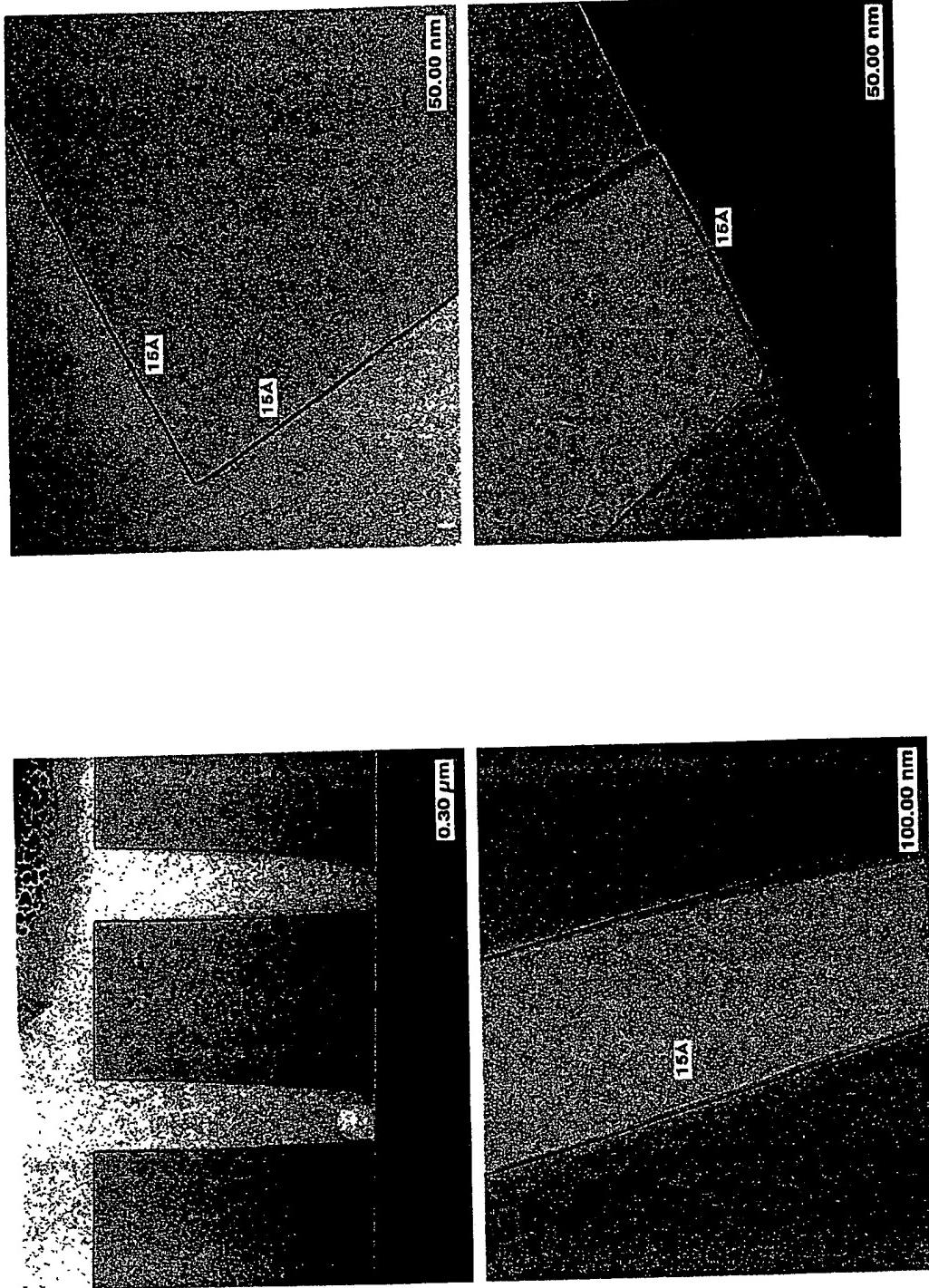
100 100 100

APPLIED MATERIALS  
ALD TaN 1001\_LC 8

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# ALD TaN IS Conformal

TECHNICAL REPORT



# Surface Roughness by AFM

Figure 10: Surface Roughness

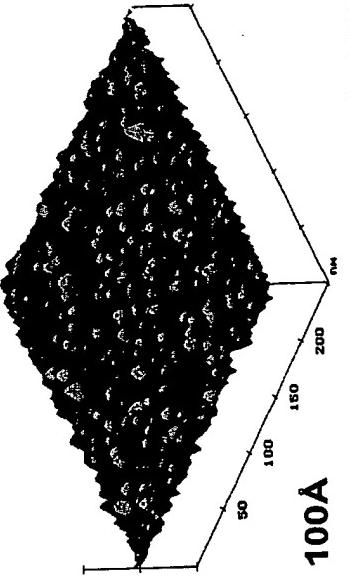
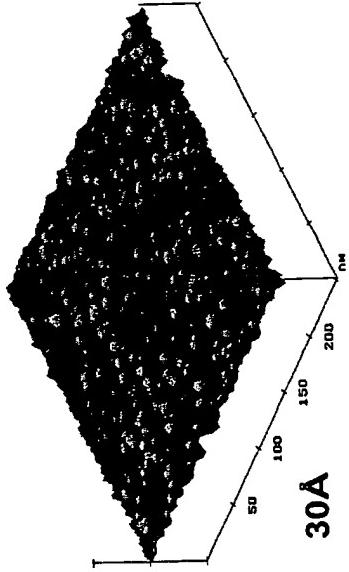
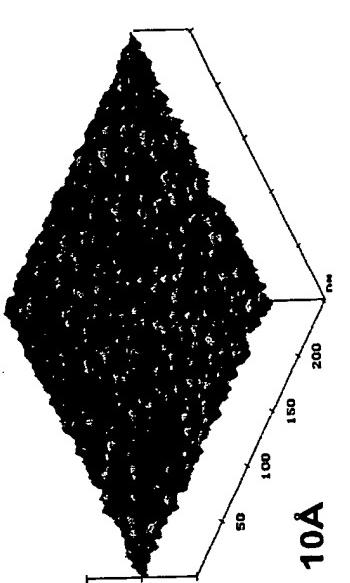
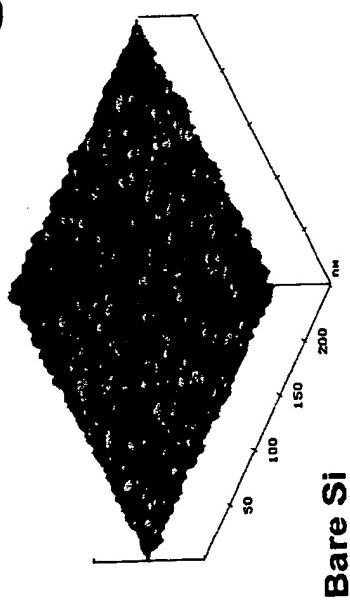
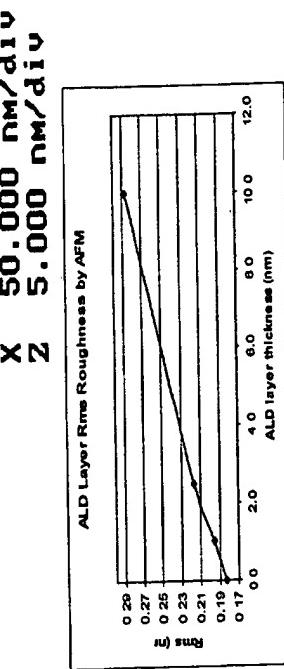


Table 1: TaN ALD layer Roughness Data

Sample	AFM Roughness (unit: nm)		
	Rrms	Ra	Rtx
100Å	0.29	0.23	3.11
30Å	0.22	0.17	2.20
10Å	0.20	0.16	1.98
Bare Si	0.18	0.15	1.65



- ALD TaN surface is smooth and pinhole free: 1 Å RMS for 100 Å film



APPLIED MATERIALS  
ALD TaN 1001\_LC\_10

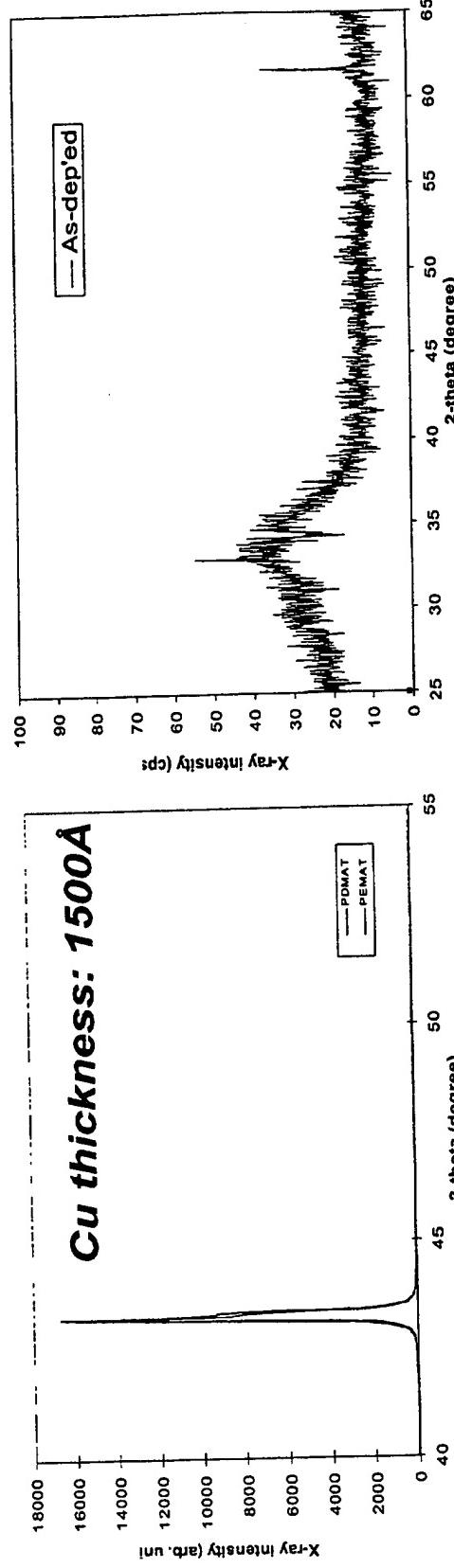
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# Film Microstructure & Cu Adhesion

புது அடிப்படை மற்றும் நிலை விழுகள்

Materials	ALD TaN Thickness	Cu Thickness	Before Scratch Surface	After Scratch Surface
ALD TaN	10A	1500A	No peeling	No peeling
ALD TaN	20A	1500A	No peeling	No peeling
oxide	0A	1500A	No peeling	

SIP Cu deposited on 10Å ALD TaN shows good adhesion



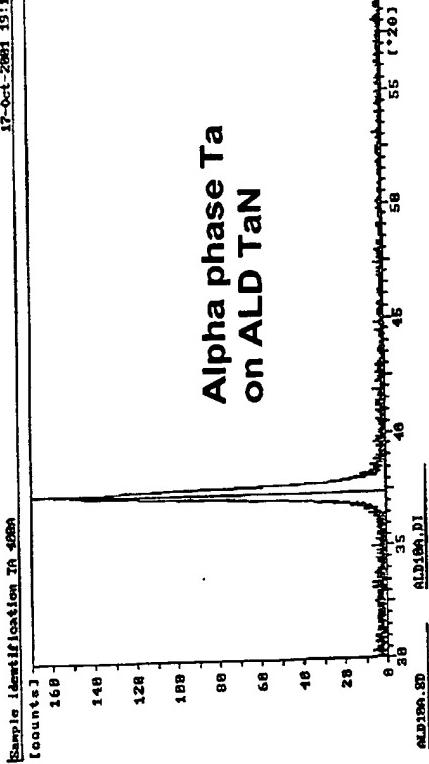
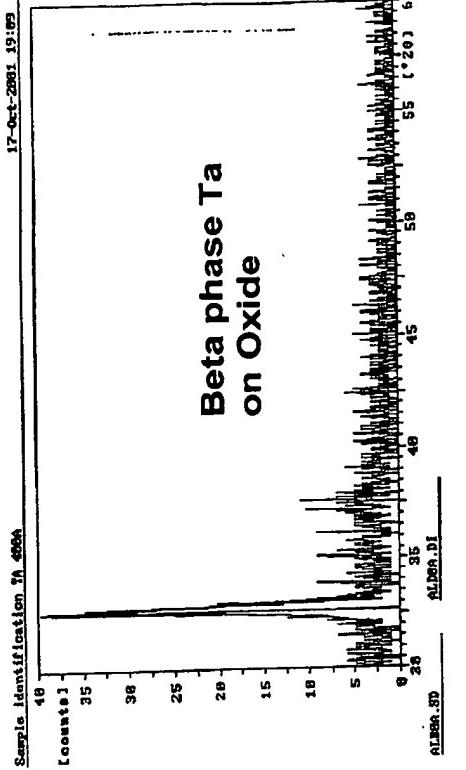
Cu seed shows preferred {111} orientation on ALD TaN

ALD TaN shows amorphous structure

# ALD TaN/PVD Ta Integration

EXCELSIOR TECHNOLOGIES

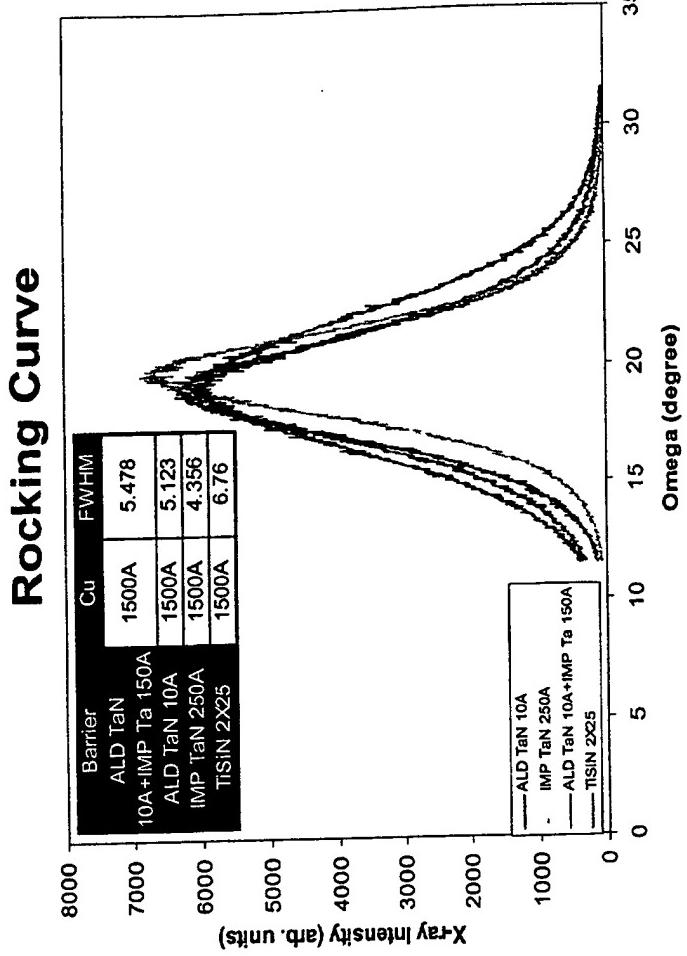
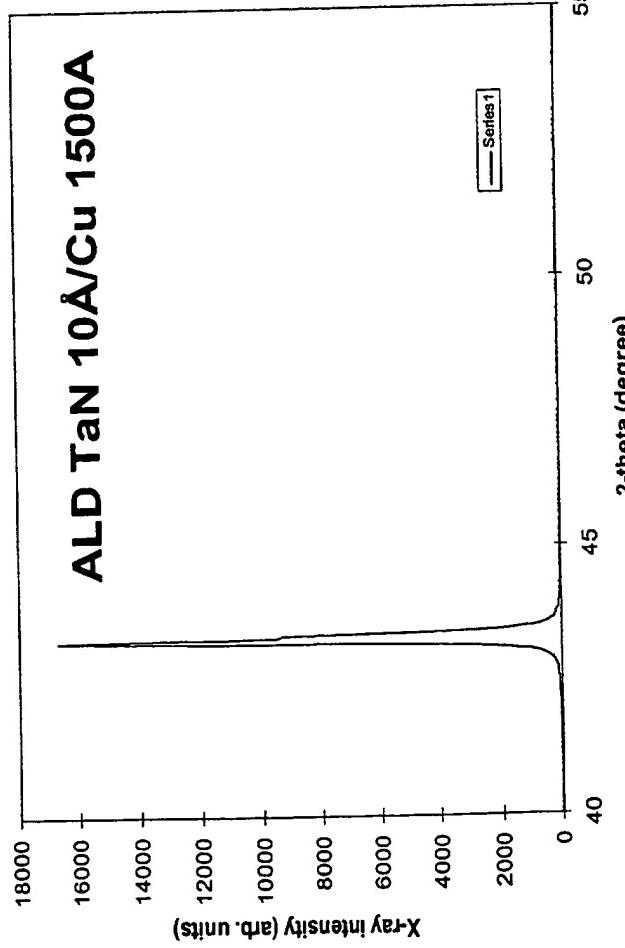
Dielectric	ALD TaN Thickness (Å)	PVD Ta Thickness (Å)	Rs	Resistivity (ohm-cm)	Rs unif. (%)
Oxide	0	150	102.2	153.3	5.8
Oxide	5	150	22.6	33.9	-----
Oxide	10	150	22.22	33.33	12.7
Oxide	0	400	33	132	5.7
Oxide	10	400	5.5	22	12.9
Oxide	50	400	6.2	24.8	12.9
Oxide	10	50	-----	-----	-----



- PVD Ta on oxide shows beta phase
- PVD Ta on very thin ALD TaN shows alpha Ta (low Rs and XRD)

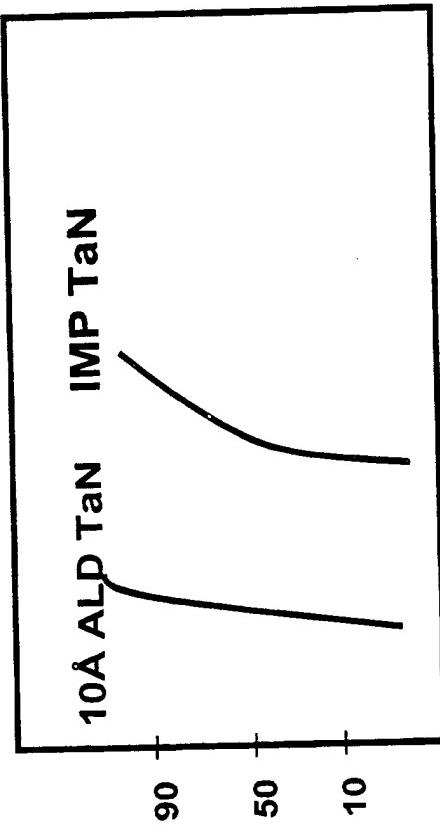
# Cu Seed Orientation

θ-2θ Scan



- PVD Cu on ALD TaN film shows (111) orientation
- PVD Cu rocking curve showed similar FWHM on the ALD TaN and PVD TaN

# ALD TaN Demonstrated Excellent Electrical Results

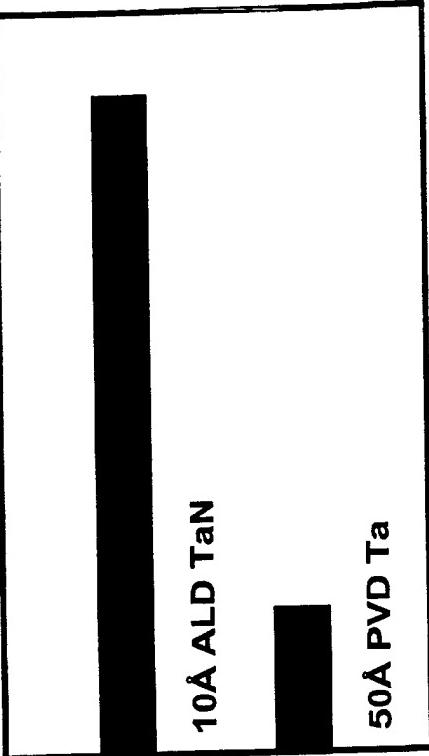


Normalized Via Resistance

- Low via resistance and tight distribution achieved for 10 Å ALD TaN

Normalized BTS Test

- 10 Å ALD TaN demonstrated >5x higher TTF compared with 50 Å PVD Ta on large test structure with 100% step coverage



Normalized BTS Test

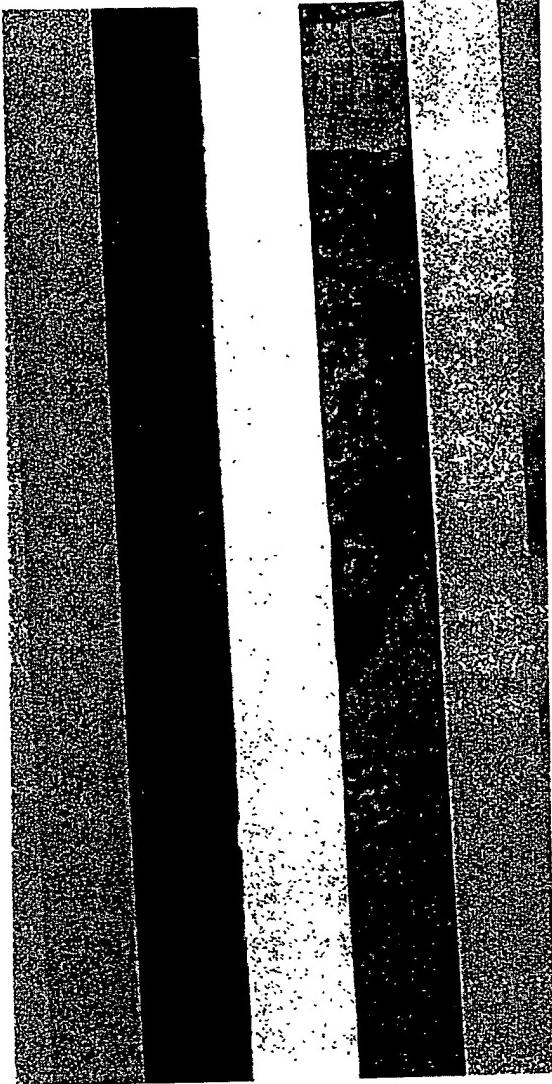
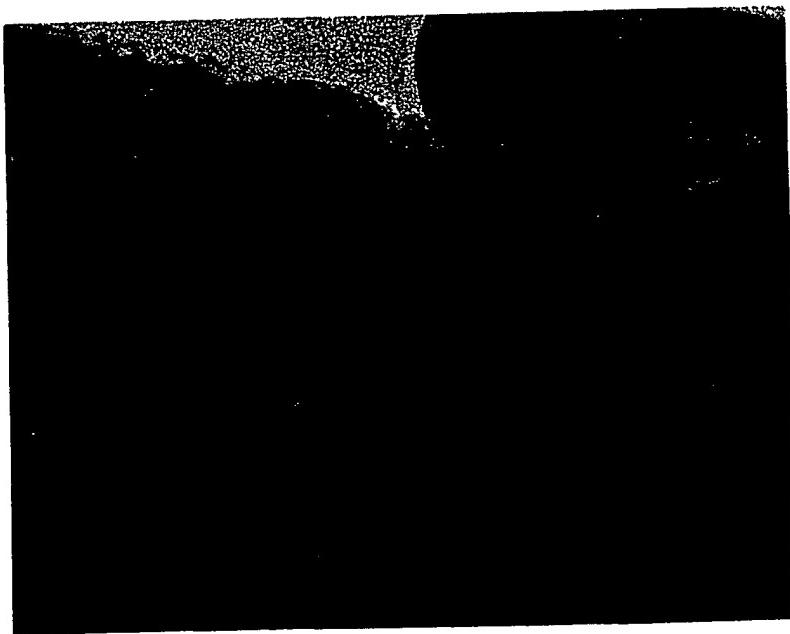
# ALD TaN Chamber Hardware

- 300mm ALD Chamber design
  - Endura XP robot compatible for high throughput
  - TxZ based chamber body
  - Small volume reaction zone
  - Complete/efficient purge
  - Uniform film across 300 mm wafer
  - Fast Controlled chemical delivery system
  - BFBE Gas Box
- 200mm C&F chamber/process achieved throughput >30 wph
- 300mm chamber Alpha release 6/02

# Summary

- ALD TaN is developed at deposition temperature between 200°C to 250 °C
- The Ta precursor shows acceptable thermal stability, reasonable quality control and preferred process window
- TEM images show the film is highly conformal.
- 10Å ALD TaN showed low contact resistance and tight spread distribution.
- The barrier performance of 10Å ALD TaN exhibited longer TTF compared with 50Å PVD Ta
- Cycle time reduction to 2s/cycle is performed by using a newly designed hardware for ALD processes. High throughput process is achievable.

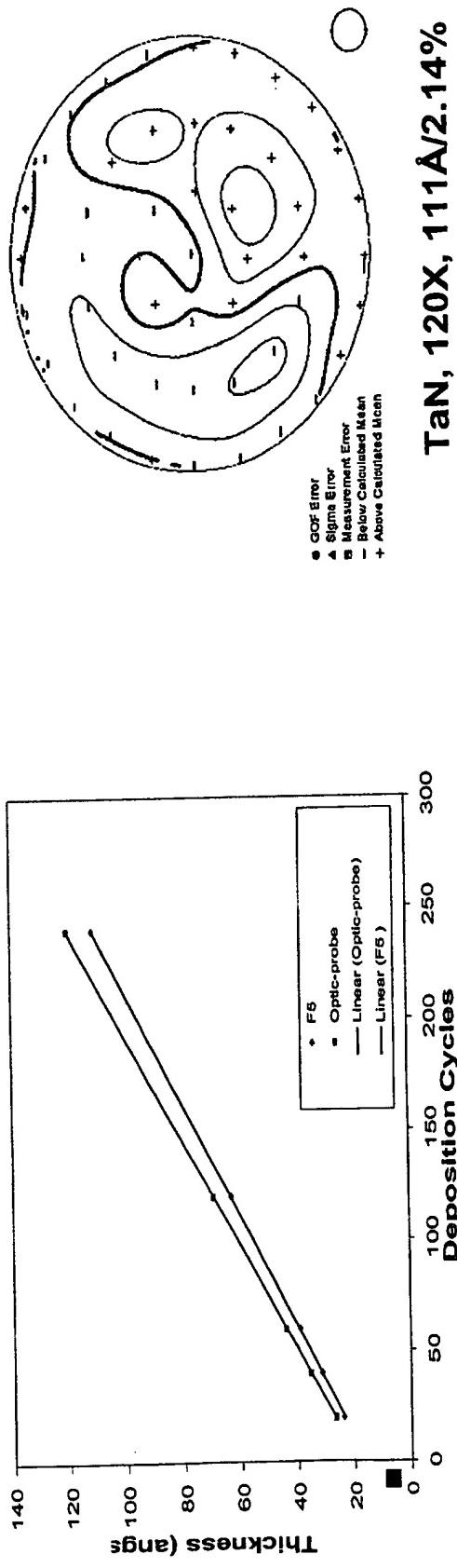
# Cu Grain Growth Across Thin Barrier



Film stack: Ta\Cu\ALD TaN\Cu

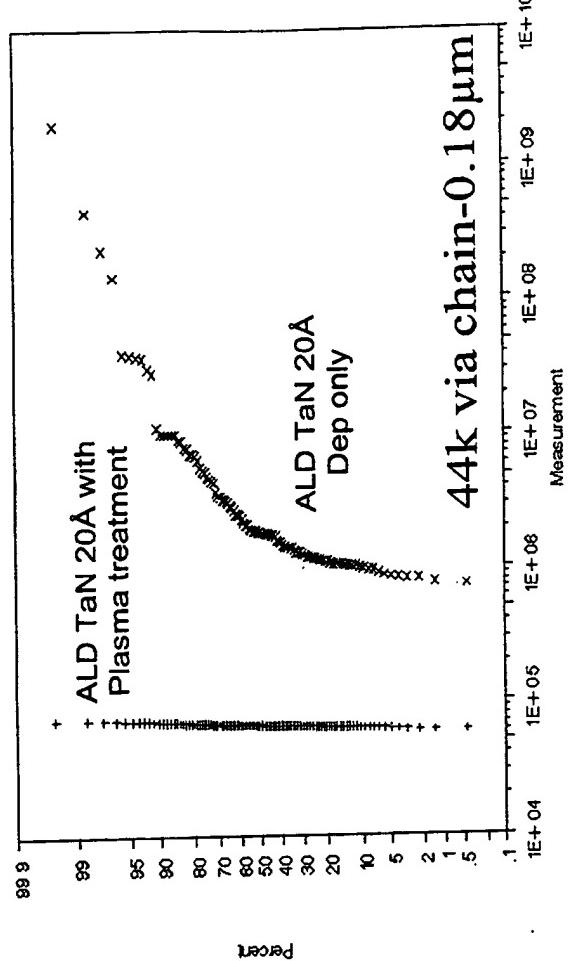
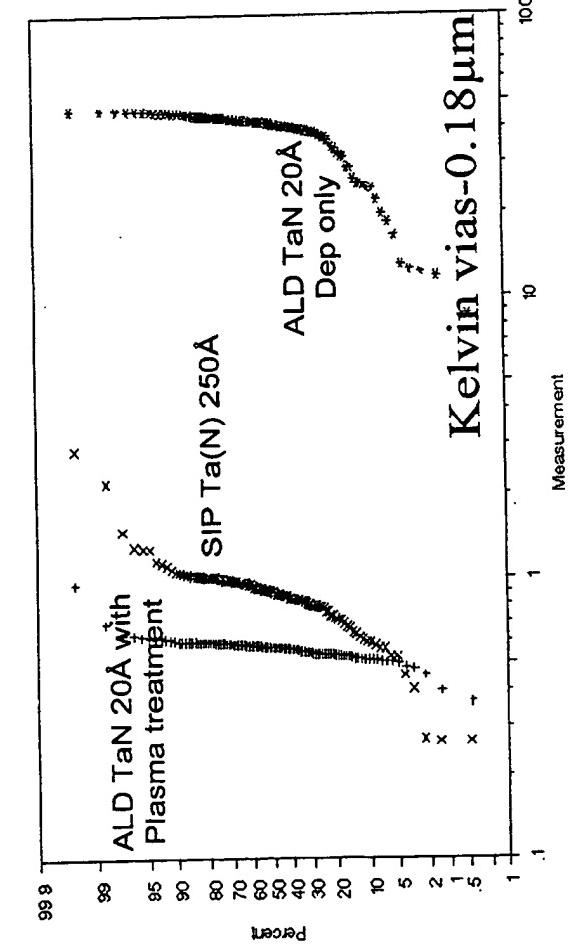
- TEM studies show that Cu grains can extend growth across barrier thickness  $\leq 15\text{\AA}$
- The cross growth appeared for both in-situ or annealed film stacks

# ALD TaN Thickness Measured by Ellipsometer



- Ellipsometry is a good tool for ALD TaN film non-uniformity measurement (both F5 and UV 1250)
- The film thickness measured correlates well with the number of the ALD cycles for film thickness  $> 20\text{\AA}$
- For  $\sim 10\text{\AA}$  film, the XRR/XRF is being evaluated

# ALD TaN Via Resistance

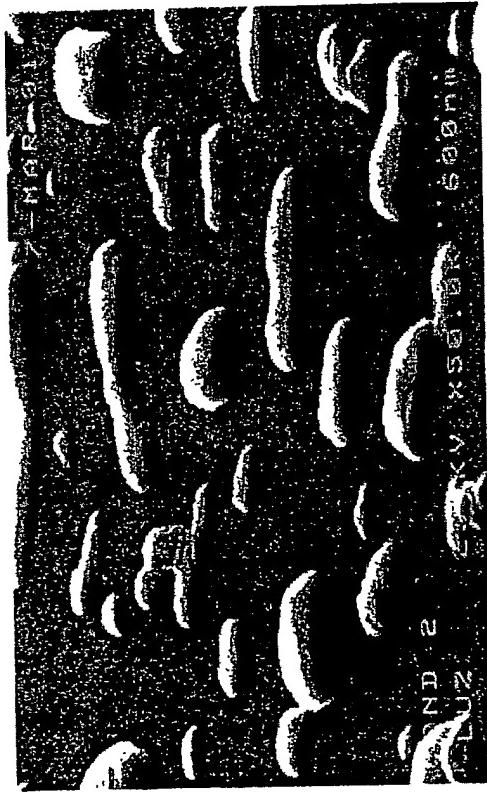


- Plasma treatment reduces ALD TaN via resistance
- Process without plasma treatment also developed to achieve low via resistance with thin ALD TaN

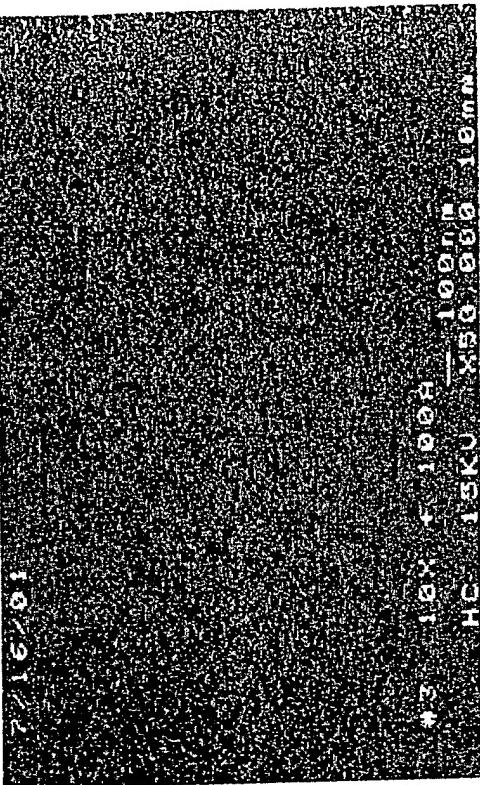
# Cu Dewetting Test on ALD TaN

Samples annealed at 380°C for 15min

100Å Cu on 10Å ALD TaN (Process I)



100ÅCu on 10Å ALD TaN (Process II)



- PVD Cu showed good wetting to ALD TaN with optimized process

EXHIBIT D - FORM 10

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**Patent Counsel**  
**Applied Materials, Inc.**  
P.O. Box 450-A  
Santa Clara, California 95052

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